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Trace metal partitioning and concentration in sediment from the St. Clair Delta, Lake St. Clair and the Detroit River, Ontario, Canada

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Trace Metal Partitioning and Concentration in Sediment from the St. Clair Delta, Lake St. Clair and the Detroit River, Ontario, Canada

By

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ABSTRACT

In this study, sediments were collected from the Detroit River – Lake Erie waterway and subjected to a sequential extraction procedure in order to evaluate the precision of the procedure and determine metal partitioning and concentrations of Pb, Zn, Ni, Cu and Cr. The samples were subjected to a three stage sequential extraction procedure. The three phases that were separated out were (1) carbonate, exchangeable and adsorbed (AEC) fraction; (2) organic material (ORG); and (3) Fe-Mn oxides (RED). Metal concentrations were determined by ICP-OES. The metal concentrations and distribution among three sediment fractions were scrutinised in the context of other sediment characteristics including grain-size, total carbon and total major element data.

Precision of certified reference materials indicated the sequential extraction procedure produced good to excellent results aside from zinc contamination within the procedure. The highest metal concentration of Pb, Cu, Zn and Cr were found in Lake St. Clair sediment at site LS17, adjacent to the shipping channels and in the deeper part of the Lake. Ni, Cu and Zn recorder higher concentrations than released in previous reports. The trace metals were primarily released from the less labile reducible step of the extraction excepting for lead which favoured the AEC step. Lower metal levels were recorded in Detroit River sediment but Detroit River sediment recorded higher proportions of the more labile metal forms.

For Walter and Kathleen,
Anna-Marie and Heather

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I acknowledge permission granted from the Walpole Island First Nation Reserve to sample channel sediments. I was supplied with guides who greatly aided in sample collection.

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CHAPTER 1

INTRODUCTION

OBJECTIVES OF THE STUDY

A standardised procedure for sediment collection, handling, and processing may provide a more informative spatial view of metal concentration and partitioning among different sediment 'phases' from locale to locale within the Lake Huron-Lake Erie waterway. This waterway, which includes the St. Clair River, Lake St. Clair, and the Detroit River, serves as a primary source of water for industrial, municipal, and recreational applications within a heavily populated and industrialised region of the Great Lakes Basin. The importance of the region with respect to its fresh water resource and evidence of recently accelerated ecological change, stresses the need for baseline biogeochemical studies and characterisation of lake and river sediment. Such studies would provide crucial data for the assessment of the changes taking place.

Previous studies of metal contaminated sediment lack standardisation with respect to (a) sampling, (sample collection, storage temperature and duration of storage vary); (b) particle size, (metals from natural and/or anthropogenic sources tend to accumulate in finer-grained fractions of sediment and enrichment examinations require compensation for grain-size); and (c) method of treatment (extraction and analysis of the extractant) (Mudroch, et al., 1988, DeGroot, et al., 1982). Without a standardised procedure, metal concentrations cannot realistically be compared on a regional basis or between different studies of the same area. One of the major weaknesses of pollution studies over the last 30 years has been the absence of international and national comparisons of heavy metal pollution because of the lack of standards for collection, preservation, analysis of

sediment and presentation of the analytical results (DeGroot, et al. , 1982). The wide range of concentrations of metals reported in Lake St. Clair and Detroit River sediments reflects the need to develop a standard sampling protocol and a standard analytical technique in assessing metal concentrations and distribution (Mudroch, et al., 1988).

The objectives of this study are two-fold: (1) to evaluate a robust and reproducible extraction procedure that may be applied to the study of trace metal partitioning in sediment, aided by direct study of the sediment residue with X-ray diffraction (XRD); and (2) to determine the partitioning and concentration of trace metal species, with particular emphasis on lead (Pb), zinc (Zn), nickel (Ni), copper (Cu), and chromium (Cr) within the sediments of the Lake St. Clair - Detroit River corridor. These metals, associated mainly with steel and petrochemical industries, are distributed due to historic and current disposal practices combined with sediment transport and deposition (Fallon and Horvath, 1985). This study also sought to examine affinities between metal concentrations and metal partitioning with major element concentration, grain-size, and Total Carbon (TC).

Without anthropogenic input, the distribution and concentration of trace metals in sediment reflects their concentration and occurrence in rocks and deposits within the drainage area. In essence, geological weathering is the source of baseline metal concentrations. Anthropogenic trace metal influx often exceeds this quantity and sediment becomes a major sink for trace metal storage in the aquatic environment. Within the Great Lakes region, major sources of metals entering the environment by way of human activity includes: industrial processing of ores and metals liberating metals by

coal burning, coke oven emission, fuel oil burning, (Singer, 1988); emission from cement manufacture; solid waste dump leachates; and animal and human by-product waste.

Previous metal studies of Great Lakes sediment employed total and partial digestions. A total digestion aggressively decomposes the entire sample including silicates and other minerals commonly resistant to weathering. Partial digestions do not completely decompose the sample; these digestions are designed to dissolve all but the silicates and resistant minerals. Both procedures produce a solution usually analysed by inductively coupled plasma emission spectrometry (ICP-OES) or atomic absorption spectrometry (AAS). Metals released from sediment by total extraction reflects the total sum of metals in all components of the sediment; metals released from partial extractions are considered the more labile forms of metals since silicate and other residual minerals are theoretically left untouched. Partial extractions are selective since the extraction partitions metals accordingly.

Only recently has research focused on phase-specific metal partitioning. Phase 'specific' alludes to the complex and heterogeneous mixture of organic and inorganic phases that make up sediment. Borrowing from geochemical exploration and soil chemistry studies, sequential extractions (SEQ) provide qualitative information on metal partitioning among these various phases occurring in sediment. Sequential extractions are selective and partial digestions. Selective extractions target metals held within specific fractions or chemical components of the sediment that serve as reaction sites for metals. Sequential extractions are 'layered' techniques whereby a sample is subjected to a succession of increasingly reactive reagents. The nature and sequence of the reagents

provides information on the partitioning of the metals into different chemical phases of the material sampled.

Though partitioning extractions are becoming the favoured analytical technique in sediment geochemistry, it is crucial to note that SEQ extractions may determine the form and association of the metal within the sediment, but this does not necessarily imply that these metal forms are primary. Though a metal may be extracted as a particular species, one should not assume that this was the metal form prior to its appearance in the aqueous system. Authigenic reactions may have also have altered the metal speciation (Filipek & Owen, 1979).

Determination of metal partitioning in sediment may provide detailed information on the origin of the metal, its mode of occurrence, biological and physicochemical availability, mobilisation and transport (Jenne, et al., 1977, Tessier, et al., 1979, Tessier et al., 1984, Miller et al., 1986 and Bendell-Young et al., 1991), allowing for more realistic assessment of future mobilisation and the threat of metal toxicity to lifeforms. Metal bioavailability, a quantitative measure of the utilisation and incorporation of metals by biota under specific conditions, has been linked to metal speciation and its concentration in sediment. The understanding of the interrelation between solid matter speciation and the extent of metal bioavailability is contentious and often contradictory in the literature. Many studies have found reliable relationships between metal concentrations in organisms and extractable metal levels in surrounding sediment (refer to Pugsley, et al., 1988, and Van Hattum et al., 1993 for summaries) but assumptions linking metal speciation with bioavailability may be unqualified since the leachable fraction may not directly correspond to the amount available to the biota. To generalise, information is

lacking on metal speciation and concentration in water and sediment with respect to the health of aquatic life.

Knowledge of metal partitioning may positively affect decisions regarding the management of trace metals in the environment. For example, guidelines concerning metal toxicity levels, dredged sediment disposal and waste disposal could be more effective if metal behaviour was understood in environmentally sensitive areas. Total metal extractions as a criteria for environmental assessment assume all metal forms have an equal environmental impact; such an assumption is untenable (Tessier, et al., 1979).

LOCATION

Locations of sediment collection sites from the St. Clair Delta, Lake St. Clair, and the Detroit River are shown on Figure 1. The area lies within the Lake Huron-Lake Erie corridor of the Great Lakes Basin of North America (Figure 2).

ST. CLAIR DELTA

The St. Clair Delta , located at the mouth of the St. Clair River (Figure 3), is the largest delta in the Great Lakes Region, covering approximately 512 km^2. The delta is comprised of numerous marshy islands within the Canadian side of the border, forming a bird's foot shape. The deltaic islands on the Canadian side, (all unceded Indian land) consist of: St. Anne, Walpole, Squirrel, Bassett and Seaway Islands; Harsen and Dickinson Islands lie within the United States. The delta is dissected by the North Channel, Middle Channel and South Channel (the international boundary between Canada and the United States is in the South Channel). Only the South Channel remains navigable to large lake freighters.

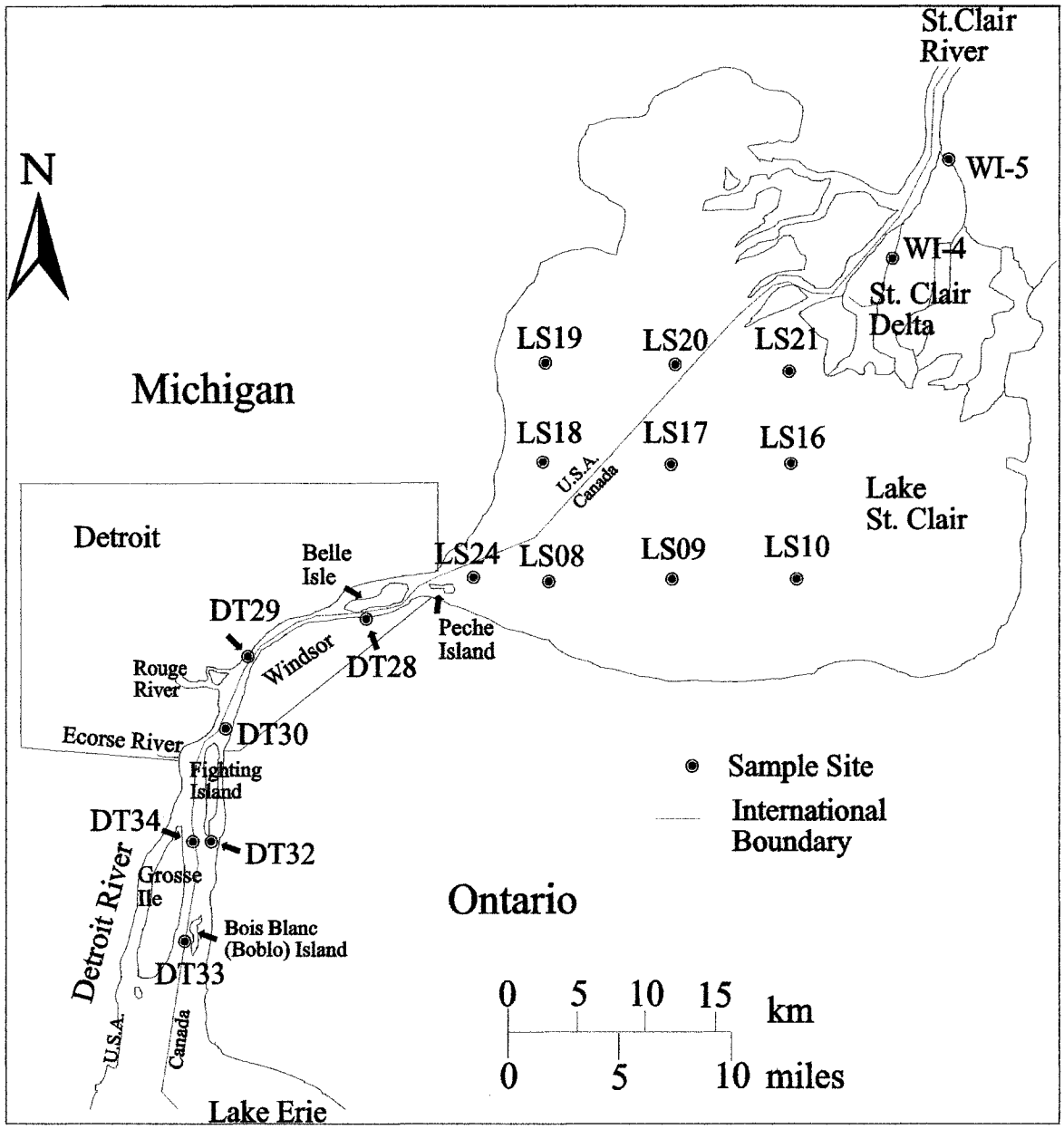

Figure 1. Sample Location in the St. Clair Delta, Lake St. Clair and the Detroit River.

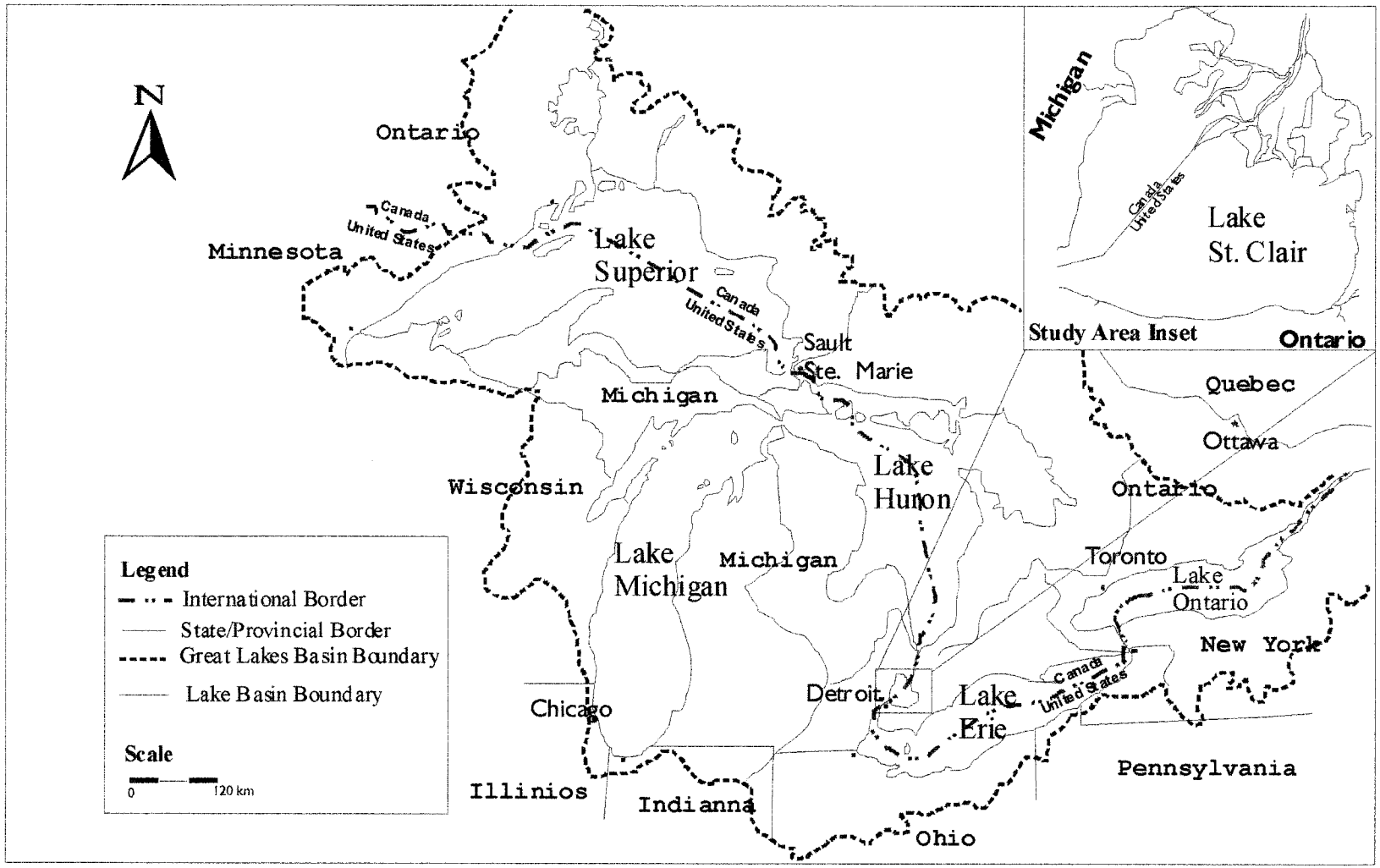

Figure 2. Regional Map of the Great Lakes Basin of North American with Study Area Inset.

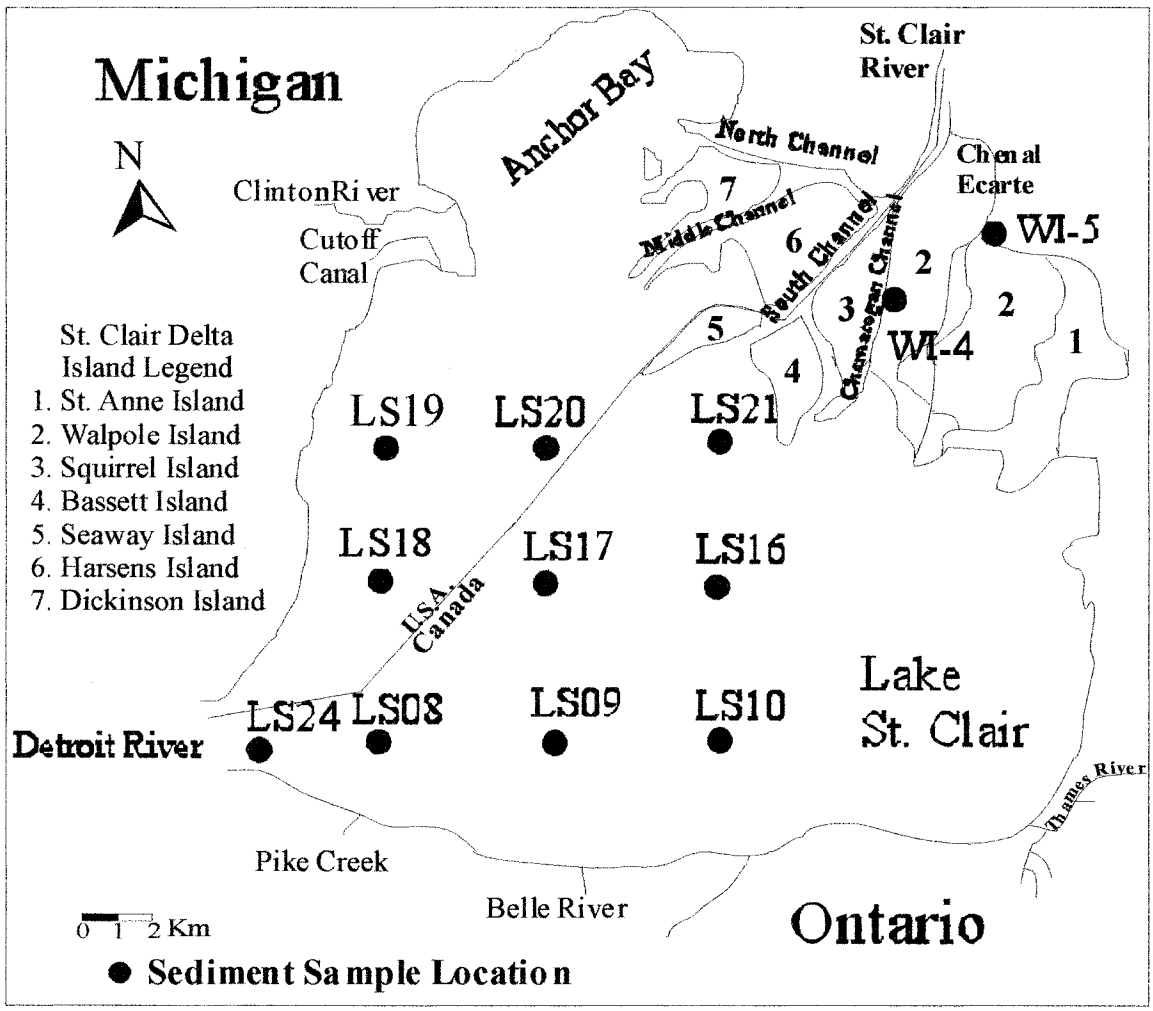

Figure 3. Detailed Sample Location Map of Lake St. Clair and the St. Clair Delta.

The more recent part of the delta fringe extending into Lake St. Clair, is marshy and low-lying. The older and sandier portions of the delta were deposited during higher water levels. The bulk of the sediment supplied to the delta was apparently sourced from wave and current erosion along the shores of Lake Huron (Taylor, 1895).

Permission was obtained from the Council of the Walpole Island Unceded Indian Territory to sample from their waterways. Two sediment samples were collected from Chenal Ecarte and the Chematogan channel (Figure 3) in the spring of 1996. These sample sites were easily accessed by road. Sediment was collected from Chenal Ecarte by suspending a ponar grab sampler from a steep embankment and sediment was obtained from the Chematogan channel by wading into the channel way.

LAKE ST. CLAIR

Lake St. Clair is a shallow, sub-circular lake located within the Lake Huron-Lake Erie corridor, with a surface area covering 1 190 km^2. The lake stretches 42 km at its longest north-south transect and 38 km east-west at its widest point. The St. Clair River is the major tributary draining into Lake St. Clair which in turn, flows into the Detroit River; the Detroit River drains into Lake Erie. The southern and eastern shorelines of Lake St. Clair are extensively urbanised whereas the marshy northern and western shorelines are flanked by farms and used for hunting purposes.

Sediment samples were collected from the lake substrate at nine locations (Figure 3) in October, 1996 with care being taken to avoid the dredged shipping channel and decommissioned sediment dumping grounds.

DETROIT RIVER

The Detroit River is a 35 km long channel forming the international boundary between Canada and the United States (Figure 4). The river flows from Lake St. Clair and drains into Lake Erie. The upper Detroit River riverbanks are extensively urbanised and are lined by municipal, recreational and industrial facilities. The lower Detroit River, especially from Zug Island southward to Grosse Ile, is an industrial valley of steel and petrochemical plants. The river is an intensive shipping route, and serves as the water source for industrial and municipal needs. Consequently, numerous industrial and municipal discharges drain into the river from both sides.

Within the river are a series of islands that are also used extensively for recreational and industrial purposes. Fighting Island and Grosse Ile have been used as disposal sites for waste products from the manufacture of caustic soda and soda ash (predominantly gypsum). Mud and Grassy Island have been used as disposal sites for dredged sediment.

Seven sediment samples were collected from the Detroit River with a ponar grab sampler in the spring of 1996. The shipping channels, obvious sewage outfalls and industrial discharges were avoided during the sampling. Areas were also selected to ensure adequate fine material for geochemical analysis.

The St. Clair River, which flows into Lake St. Clair from Lake Huron, was sampled in the spring of 1996, but the collected material lacked sufficient quantities of a fine-grained fraction (< 63 μm) needed for the geochemical analysis. The fine-grained fraction was required for this study in order to normalise the variability of sediment

textures from the fluvial to lacustrine environment. The sediment in the St. Clair riverbed consisted of very well-sorted and rounded quartz and carbonate grains.

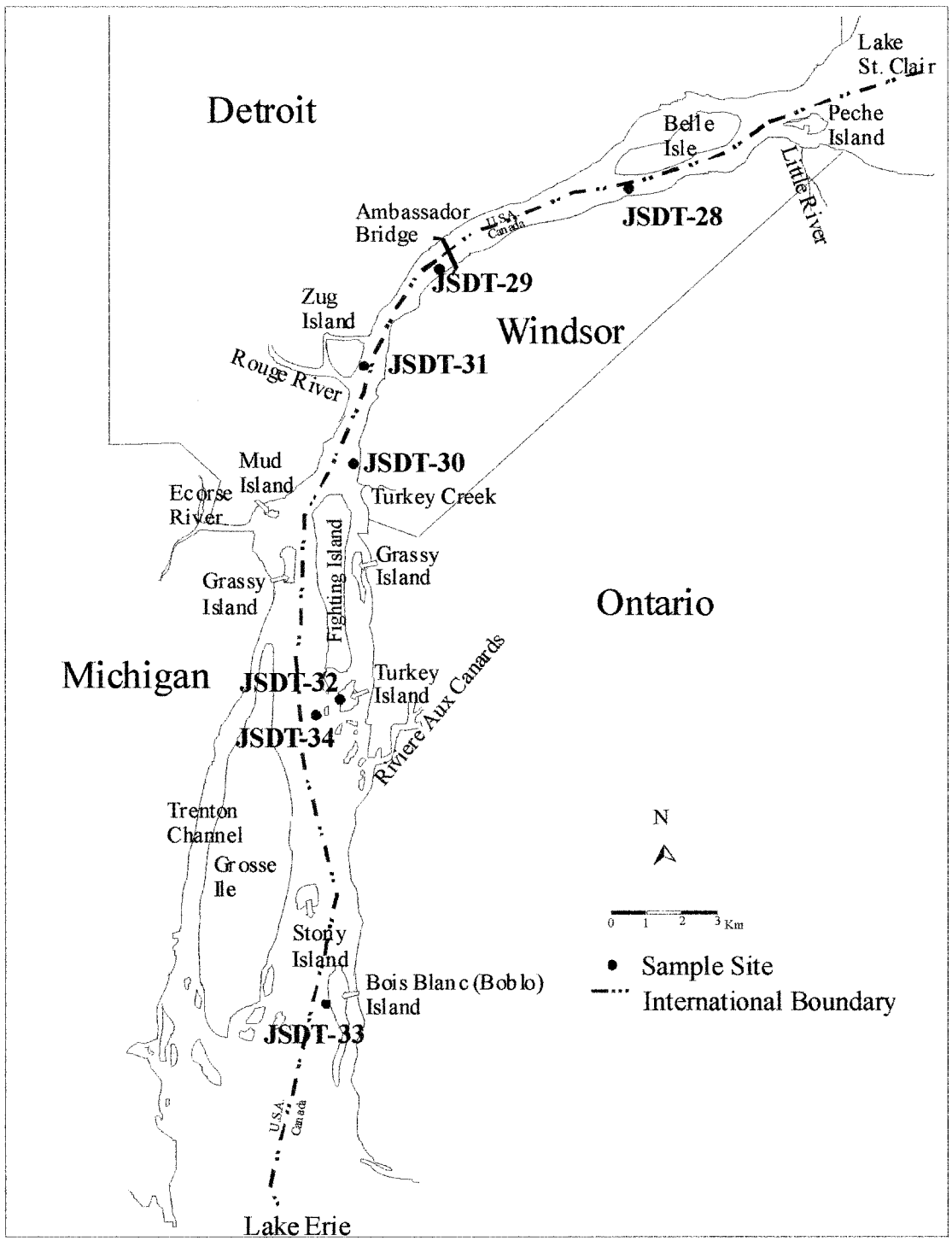

Figure 4. Detailed Sample Location Map of the Detroit River.

CHAPTER 2

REVIEW OF THE LAKE ST. CLAIR - LAKE ERIE WATERWAY

Sediment is defined as the settled dregs at the bottom of a liquid (Collins English Dictionary, 1986 Edition). Aside from this simplistic definition, sediment is a mixture of allochthonous and autochthonous organic and inorganic material including chemical precipitates. Transported material includes the products of weathering and erosion, (weathered debris from outcrop, glacial deposits and soil), organic material, and atmospheric and waterborne inputs (anthropogenic or otherwise). In situ materials may include authigenic minerals and biomatter.

GEOLOGICAL BACKGROUND

Sediment in the rivers and lakes of southern Ontario should be discussed in context of regional geology, geomorphology and cultural geography. Considering that the sediments of Lake Ontario and Lake Erie contain 90 to 99% mineral matter (Thomas et al. 1972, 1976, Kemp and Dell, 1976), the local and regional geology and geomorphology define the nature of the sediment.

REGIONAL BEDROCK GEOLOGY

The bedrock geology of the Great Lakes region consists primarily of Palaeozoic sedimentary assemblages overlapping a crystalline Precambrian basement exposed in the northernmost reaches of the Great Lakes Basin (Figure 5). The metamorphosed assemblage of sedimentary and igneous suites of the Precambrian basement underlie a relatively unaltered Palaeozoic veneer of limestone, shale, dolomite and sandstone in south-western Ontario (Figure 5).

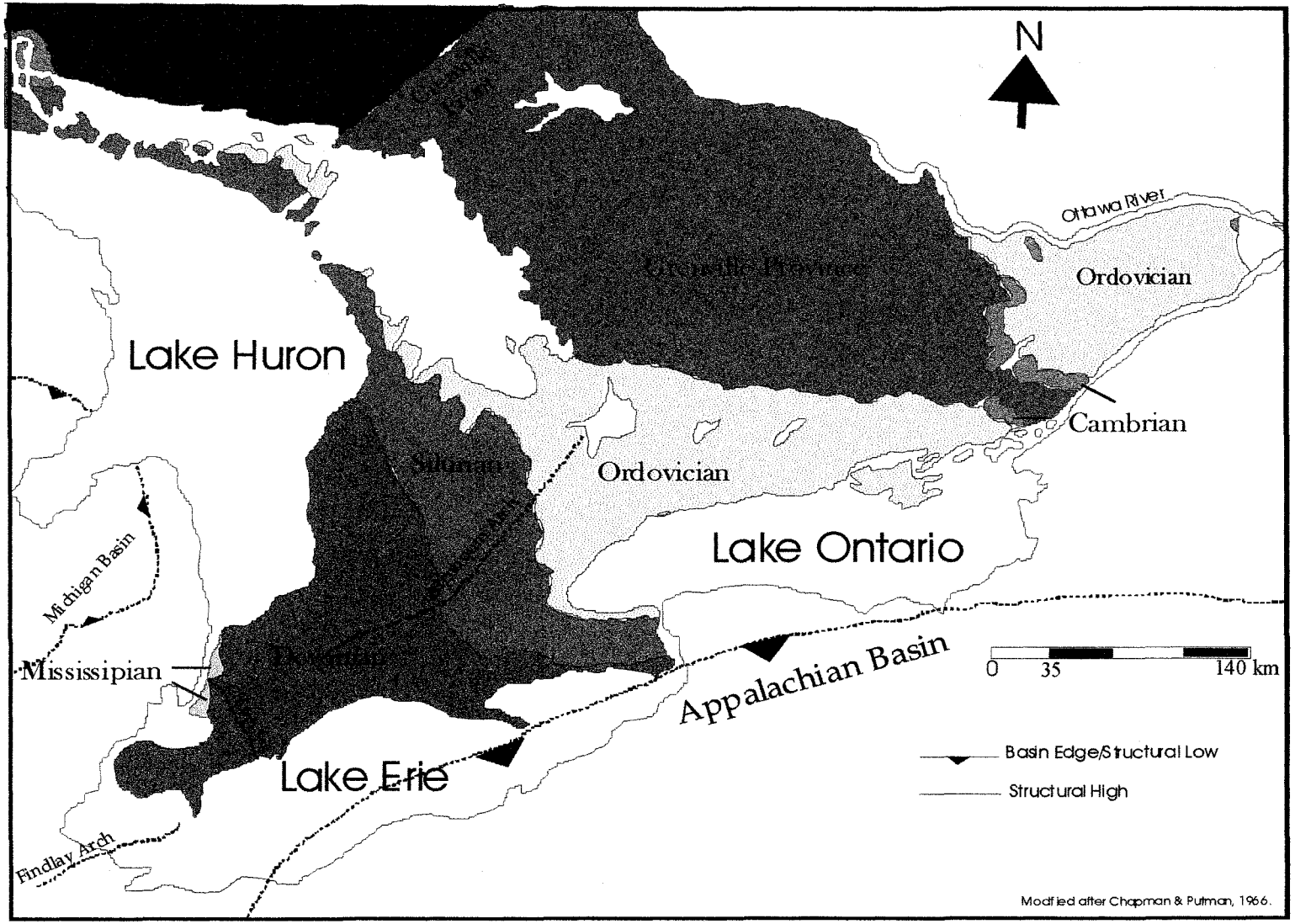

Figure 5. Regional Bedrock Geology of the Great Lakes Area.

PRECAMBRIAN ROCKS OF THE GRENVILLE PROVINCE

The cratonic Precambrian basement consists of highly deformed and metamorphosed assemblages of the Central Gneiss and Central Metasedimentary belts of the Grenville Structural province, and the Superior Structural province, outcropping east and north of Georgian Bay. The Grenville province is the root of a 1.0 - 1.1 billion year old mountain chain of ancient metasedimentary and metavolcanic suites. Prior to the inundation by Palaeozoic seas, erosion and weathering flattened the craton's surface to a peneplain during the 400 million year hiatus between the Grenville Orogeny and deposition of the oldest Palaeozoic sediments (Carter et al., 1993). A record of the erosional interval, a Precambrian regolith, survives in places between the craton and the Palaeozoic cover.

The craton remained stable during the post-Precambrian period. The development of the Michigan and Appalachian basins and the surrounding highland arches were formed by mild vertical tectonics (Martini, et al., 1970). The Algonquin Arch, a basement high trending south-west, is the dividing line between north-west dipping sedimentary sequences in the Michigan Basin and the south-easterly sedimentary sequences dipping gently into the Appalachian Basin (Figure 5). This positive structural element provided a gentle syncline for the deposition of the Palaeozoic sequences.

PALAEOZOIC ASSEMBLAGES

Most of the Great Lakes Basin is underlain by Palaeozoic marine sequences of Cambrian, Ordovician, Silurian, Devonian and sporadic Mississipian-aged rocks. Series of marine transgressions and regressions during the Appalachian Orogeny deposited terrestrial and marine sediments. Lithologically, these sequences are primarily composed

of limestone, dolomite, shale, sandstone, halite, and gypsum. Cambrian rocks, with a maximum thickness of 165 m, outcrop primarily as scattered sandstone remnants. Ordovician-aged rocks, exposed north of Lake Ontario and at the southern area of Georgian Bay, obtain thickness up to 920m. Lithologically, the Ordovician deposits vary from shale, interbedded limey shale with limestone, limestone, dolomite and sandstone. Silurian strata, consisting primarily of dolomite with minor shale, gypsum and halite, defines the escarpment in southern Ontario angling from the Niagara River to Manitoulin Island and westward. The maximum subsurface thickness is up to 620 m for Silurian sedimentary rocks. Shale, sandstone, limestone and dolomite dominate Devonian deposits which range up to 390 m in thickness (Telford, 1975). The drainage basin for Lake St. Clair and the Detroit River overlie the Middle Devonian (limestone, dolomite and shale), Upper Devonian shale and Mississipian to Devonian shale (Ontario Geological Survey Map 2418).

PLEISTOCENE GLACIATION

The topographically challenged region draining into Lake St. Clair and the Detroit River has no surface exposure of rock. The drainage basins of Lake St. Clair and the Detroit River, lie within the late Quaternary deposits (up to 92 m in thickness) deposited during the Pleistocene glaciation (Pezzetta, 1968). The last one million years have drastically altered the topography of southern Ontario; the surficial sediment and landforms are a product of the last major ice advance and retreat during the Wisconsinan Stage when gigantic ice sheets invaded from Labrador and the Quebec highlands with 4 lobes emanating from and retreating to the depressions occupied today by Lake Ontario, Lake Erie, the central part of Lake Huron and Georgian Bay. The distribution of

moraines, drumlins, eskers and ancient shorelines delineate the minor physiographic regions of south-western Ontario today (Martini, et al., 1970, Barnett, 1992).

Within the study area, a belt of late to post-glacial lake-bottom clays and sand plains and spillways mark the top of the regional stratigraphic sequence (Stone and Saunderson, 1992). Thin sand deposits rim the easterly and south shore of Lake St. Clair and the banks of the upper Detroit River (Energy, Mines and Resources Map, 1972). Extensive clay plains encircle these sand deposits; glacial clays are also found along the lower St. Clair River and the drainage area of the lower Detroit River. The islands of the Detroit River, aside from the dredged sediment of the channels, consist of glacial clays (Chapman and Putnam, 1984). The local soils, predominantly Orthic Humic Cleysol and Gleyed Grey-Brown Luvisol soils, are products of the last 10 000 years of soil evolution.

PHYSIOGRAPHIC AND HYDROLOGIC FEATURES

ST. CLAIR RIVER AND ST. CLAIR DELTA

The St. Clair Delta is the largest delta in the Great Lakes Region and is located at the mouth of the St. Clair River (the outlet of Lake Huron). The St. Clair River, with its high flow rate, averaging about 5 000 m^3/s (Korkigian, 1963), inhibits the deposition of fine-grained material on its bottom; the fast flowing river is incising downward into hard consolidated glacial clays and finer-grained silt clays (Rukavina, 1986). Firm, hard, glacial lacustrine clays were found to exist in some areas of the river channel (Sly et al., 1972). Sediment transported along the St. Clair River substrate consists of these eroding glacial clays and medium to coarse sands and gravels (Mudroch and Hill, 1975).

The deltaic islands of the St. Clair Delta wedge outward onto the glacial lacustrine clays and silts of the Lake St. Clair substrate. Only the western part of the delta is actively forming today, fed by sediment transported by the St. Clair River branching into three distributary channels referred to as the North, Middle and South channels (Herdendorf and Raphael, 1986).

Within the last 10 000 years, low lake levels due to opening northerly outlets for glacial waters, exposed the St. Clair Clay Plains and within 5 000 years, deposition of the 'premodern' delta ensued. Premodern deltaic sediments consist of coarse sands. A lowering of Lake St. Clair 3 500 years ago resulted in the growth of the modern delta, composed of silty sand to sandy clay, at an elevation of 2 m below the 'premodern' delta (Cummings, 1995).

LAKE ST. CLAIR

Lake St. Clair (Figure 3) is a sub-circular body of water with 438 km of shoreline. The lake is very shallow; sampling at the lake centre during the fall of 1996 indicated that the lake did not exceed 7.5 m in depth in the shipping channel. The maximum depth of the lake is marked by the dredged navigation channel extending from the St. Clair River to the headwaters of the Detroit River. An average depth of 1 m was recorded by sampling in this study. Because of its small size and shallow depth, the water retention time is very low, on average 9.2 days (Herdendorf and Raphael, 1986) and therefore the water warms and cools rapidly. The development of a thermocline may not be as important in basin dynamics as with the adjacent, deeper Great Lakes.

Drainage into Lake St. Clair includes the St. Clair River, and on the Canadian side, the Syndenham and Thames Rivers. The Syndenham River drains Lambton and

Middesex counties in Ontario, funnelling water and sediment from almost 1000 square miles of a glacial clay plain (Chapman and Putnam, 1966). The Thames River drains an area of 2,200 square miles of clay plains downstream of London, Ontario and till plains and moraines upstream (Chapman and Putnam, 1966).

The pattern of recent sediment accumulation in Lake St. Clair conforms to lake bathymetry; the thickest sediments have accumulated at the lake centre. However, Lake St. Clair is considered to be a non-depositional lake. The average post-glacial sediment thickness outside of the delta is minimal, ranging from 3.5 to 7 cm (Thomas et al., 1975, Mudroch and Hill, 1975). Cs-137 dating indicated stratigraphic inhomogeneity in the sediment; recent sediment has mixed with older sediment. Cs-137 dating also determined the sediment to be 8% efficient in retaining the tracer, (only 8% of the Cs-137 that entered the sediment, based on cesium 137 results in core studies, is currently stored in the sediment) implying a resident time of approximately 3 to 6 years (J. Robbins, Great Lakes Environmental Research Laboratory, Ann Arbor, MI referenced through Rossmann (1988). The bulk of the sediment in Lake St. Clair is transported rapidly downstream to Lake Erie.

The bulk of the sediment entering the Lake Huron-Lake Erie corridor via Lake Huron is transported relatively swiftly through the St Clair River, Lake St. Clair and the Detroit River (Rossman, 1988). Thomas (1974) reached a similar conclusion in his study of mercury-enriched particles entering Lake St. Clair via the St. Clair River. Fine-grained sediment eroded from shore and bottom deposits must be subsequently carried downstream into the Detroit River. Glacial-lacustrine sediment underlying recent sediments in the lake basin is characterised by its appearance and geochemical

composition (Mudroch and Hill, 1975). The glacial lacustrine clays have lower SiO_2, CaO, and higher Al_2O_3, Fe_2O_3, TiO_2 content than the surface sediment suggesting the older sediment is higher in clay minerals whereas quartz and carbonate minerals dominate the younger sediment. Mudroch and Hill (1975) suggested the 'older' glacial lacustrine sediment has higher concentrations of well-crystallised minerals visually represented by a finer grain-size, light grey colour, sticky and firm consistency and low water content. Rossmann (1988) confirmed with core analysis that the cohesive glacial clays were easily distinguished between the overlying non-cohesive silts and clays, serving as a marker for post-settlement sediments.

DETROIT RIVER

Tributaries draining into the Lower Detroit River include the Rouge River and the Ecorse River on the American side and Turkey Creek and River Canard on the Canadian shoreline. Other than sediment transported from Lake St. Clair, the Rouge River contributes the bulk of the fine sediment entering the waterway. The Detroit River has an average flow rate of 5,600 m^3/s (Fallon and Horvath, 1985).

Detroit River sediment consists of quartz, with minor feldspars, carbonates, and clay minerals (dominated by illite, chlorite, and kaolinite). Quartz and calcite dominate the sediment, especially the > 63 μm grain-size fraction while dolomite and feldspars were found in greater quantities in the < 63 μm fraction (Mudroch, 1985). The Rouge River and Lake St. Clair supply virtually all the fine-grained sediment entering the Detroit River. The riverbed is variable, consisting of firm glacio-lacustrine clays, recent fine to silty clays, and sand to gravel along the channel. Fine-grained sediment is accumulating around Fighting Island, the confluence of the Ecorse and Rouge Rivers, and

at the mouth of the Detroit River (Hamdy and Post, 1985). Sand and gravel predominate in the channels and along Windsor and Detroit waterfronts.

CULTURAL INFLUENCES

The Great Lakes region is one of the most heavily settled and industrialised in North America. The Great Lakes are an important source of freshwater regionally and on a global scale as the lakes contain 18% to 20% of the fresh water reserves on the planet. The Great Lakes Basin also serves as a major eastern shipping route for agricultural products and natural resources including iron ore, limestone and coal. It was this access to resources and fresh water that opened the area to intense urbanisation and industrialisation resulting in loss of habitat and organic and inorganic contamination. More than 95% of the original wetland along the Detroit River has been destroyed since the early 1900's.

Years of cumulative point and diffuse sources of contamination threaten the region today. Metals and other pollutants have been introduced into the system by anthropogenic activities (Canadian and American inputs), namely: sewage overflow, municipal and industrial wastes, storm water runoff and inputs from tributaries. Air deposition and resuspension of sediments are also factors of metal introduction and transport.

PREVIOUS GEOCHEMICAL MONITORING

The majority of pollutant studies in the Great Lakes region have focused on contaminated sediment and water within the Great Lakes (Thomas, 1972, Wolery & Walters, 1974, Thomas et al. 1976, Kemp and Dell, 1976, Kemp et al., 1976). By

comparison, sediments in the connecting waterways do not possess the bank of geochemical and sedimentological data as extensive as the Great Lakes. Sediment and water quality studies of Lake St. Clair and the Detroit River drew attention in the early 1970's, when a commercial fishing ban on Lake Erie pointed the finger at water and sediment quality upstream of the western basin of Lake Erie. Noted studies of Detroit River sediment quality include Thornley et al., 1983, Thornley et al., 1984, Mudroch, 1985, Lum et al., 1985, Hamdy et al., 1985, Fallon et al., 1985, and Theis et al., 1988. Lake St. Clair sediment quality has been studied by Thomas et al., 1975 and Rossman, 1988. The wide range of metal concentrations reported in the literature for Lake St. Clair and Detroit River sediment reflects the different sampling techniques, sites and methodology used in sample preparation and analysis. Despite the range in metal values, metal concentrations are significantly elevated with respect to pre-settlement values. The Detroit River and the Lake St. Clair area have become one of the most heavily impacted ecosystems within the Great Lakes Basin (IJC, 1981, 1982, 1987, Great Lakes Quality Board, 1983, 1985)

LAKE ST. CLAIR

Studies of Hg contamination on Lake St. Clair sediment are more numerous than other trace metal or organic contaminant studies. Mercury-poisoned fish were discovered in the lake 1969 and in 1971 a commercial fishing ban was enforced. Since then, studies have correlated Hg inputs with the local chlor-alkali industries centred in Sarnia, Ontario and Wyandotte, Michigan. Though the plants were in operation since 1939 (Wyandotte) and 1947 (Sarnia), signs of serious contamination did not surface until the late 1960's –

early 1970's along the St. Clair – Detroit River system and the western basin of Lake Erie (Thomas, et al., 1974, Wolery, et al., 1974, Mudroch and Hill, 1975).

The earliest look at trace metal concentrations in Lake St. Clair was by Thomas et al (1975) who reported metal concentrations based on fifty sites sampled in 1974. Rossman (1988) examined sediment cores from Lake St. Clair for trace metals, organic contaminants, total carbon, major elements and Cs-137/Pb-210 activity to determine the pollutants stored in the sediment and estimate the quantities and permanence of the storage. Sediment grain-size was determined in the field by the 'eyeball' process. Cores were dissected, frozen, and prior to metal analysis, freeze-dried for digestion in HCl-matrix. The largest mass of anthropogenic metals, (predominantly Pb, Zn, Ni, Cu and Cr) were temporarily confined to the depositional basins (primarily the lake centre and the northernmost bay).

A survey of surface sediment trace metal concentrations was compiled by Mudroch et al., (1988) for the Great Lakes sediment. The following data was collected for Lake St. Clair sediment (in μg/g):

Table 1. Previous Studies Summary of Trace Metal Concentrations in Lake St Clair Sediment (μg/g):

	Pb	Zn	Ni	Cu	Cr
Depositional basin	7-67	8-107	5-43	2-48	1-275
Harbour	1-52	9-132	2-35	1-54	12-155
Rivermouth (St. Clair River)	12-151	31-330	8-50	5-80	6-78

*Modified after Mudroch et al., (1988)

DETROIT RIVER

Metal concentrations are of concern to both countries that utilise the water resource. The U.S. Environmental Protection Agency began sampling sediment in the Detroit River during 1969 to 1973 for trace metal determinations. In 1970 and in 1980, the Ontario Ministry of the Environment (MOE) carried out a surficial sediment sampling program to determine trace organic and metal concentrations in the Detroit River sediment. In the Canadian study, sediment was collected with a Shipek dredge and the top 3 cm were scraped off for analysis. A HCl/HNO_3 digestion on the bulk sample was used to liberate acid extractable metals. With data released from the 1980 MOE survey, Thornley et al., (1984) concluded continuous sources are responsible for metallic contamination on the American side (primarily diffuse input from the Ecorse and Rouge Rivers) whereas point sources are more important along the Canadian shoreline (mouth of the Little River and the city of Windsor waterfront).

Lum et al., (1985) analysed the top 3 to 5 cm of bottom sediment from the Detroit River for trace metals complimented with a study of mineralogical phases. Bulk sediments were stored at 4°C and until the wet sediment was digested with HCl (to extract the chemically non-specific phase of metal) and the remainder subjected to a total extraction. The distribution of HCl-extractable and total metal concentrations indicated grain-size difference did not enhance metal accumulation. Metals were grouped according to major element association: Cd, Zn, Co Pb, Cr, Mn, and P were associated with Fe oxides whereas Cu concentrations increased with Al content. The most contaminated sediment was 2.5 km south-east Pte. Mouilee, U.S.A., 300 m north of a dumping ground, north of the confluence of the Detroit River and Lake Erie. The highest

Cu concentrations (total) were downstream from the Rouge River. As with Mudroch et al., (1985), Lum et al., (1985) also found a strong correlation between iron and phosphorous.

Mudroch (1985) investigated the concentration of trace metals and their distribution among various size fractions within the sediment and their association with major element concentration, grain-size distribution, organic carbon and mineralogical composition. Trace metal concentrations were determined by total fusion after freeze-drying and grinding the sediment. The pattern of metal accumulation determined from this study were similar to Thornley et al., (1984); both had also noted that some trace metals originated from the same source. High trace metal concentrations mark the downstream route of waters from the Rouge and Ecorse Rivers, most notably copper, zinc, and lead from the Rouge River. High zinc and lead contamination was reported along the Windsor waterfront south of Belle Isle. The grain-size study indicated trace metals accumulated in the < 63 μm grain-size fraction. No correlation was found between organic C and trace metals.

CHAPTER 3

THE NATURE OF THE SEDIMENT-AQUEOUS INTERFACE

TRACE METALS IN THE AQUEOUS ENVIRONMENT

Research in contaminated sediment evolved with the idea that sediment reflects the physical, chemical and biological conditions of the waterway (Zullig, 1956). Sediments are both a source and a sink for trace metals within an aqueous environment. The extent of metal accumulation and release from sediment is determined by a complex interplay among the physical, chemical and biological conditions. Different components within the sediment include the geological products of weathering and erosion, organic matter, authigenic precipitates, and other air and waterborne particulates. These components provide the reaction sites to which trace metals adhere and depending on the mechanism of adherence, the metal or metal species may be tightly incorporated or loosely held. The knowledge of the chemical form of metal association with sediment is necessary for estimating physiochemical reactivity and bioavailability (Stumm and Bilinski, 1972, Jenne and Luoma, 1977, Tessier et al., 1980).

Trace metals associated with particulate material may be: i) adsorbed on particle surfaces, ii) included within carbonate mineral lattice or co-precipitated with carbonate phases, iii) occluded in or precipitated within Fe/Mn oxides, iv) bound in living or detrital organic matter , v) incorporated in amorphous to crystalline authigenic sulphides, and vi) locked in lattice positions in aluminosilicates, resistant oxides or resistant sulphides (Campbell et al., 1987). Determination of metal partitioning within sediment may be approached in two ways: in principle, partitioning may be determined by thermodynamic calculations provided equilibrium exists (cf. to Tessier et al., 1985,

Luoma et al., 1983, and Oakley et al., 1987), or by experimental techniques. At the present time, thermodynamic data needed to handle the sediment-water interface is incomplete; a complex variety of solid phases binding metals make it difficult, if not impossible, to directly determine sediment-metal association as well as the amorphous nature of phases involved and low metal concentrations (Campbell et al., 1987). As a result, experimental techniques are currently at the forefront in speciation studies.

Since adsorption onto particles is the primary factor in transport, deposition, reactivity and toxicity of metals, geochemical sediment analysis should reflect the chemistry of the particle surface. With this in mind, there are three methodological concepts for examining the distribution of trace metals (Keyser, et al, 1978, Fergusson, 1990): (1) separation of sediment fractions by mechanical means (based on size, density or magnetic properties); (2) direct study of the surface of the particles by such techniques as electron microprobe X-ray emission spectrometry (EMP), Auger electron spectrometry (AES), and secondary ion mass spectrometry (SIMS); and (3) solvent leaching of bulk sediments or particle fractions. By employing the last method of study, determination of the metals in sediment involves extracting the desired metal form and chemical analysis of the extractant.

The greater part of dissolved metals, under normal physicochemical conditions, will rapidly adsorb onto particulate material. If the sediment phase has strong adsorptive power, the metal is securely held at the surface by physicochemial bonding or incorporation. If the phases possess weak bonding abilities, metals may shift between different sediment components with time. The partitioning behaviour of the metals and

the organic and inorganic phases is dependent on the chemical, geological and biological environment.

Trace metals occur in dissolved, colloidal or particulate form and each has inherent biogeochemical properties attributing to their mobility and bioavailability. Metal mobility and cycling is a function of: 1) the properties of the trace metals, such as solubility, reactivity for complexation and adsorption; 2) solution characteristics such as pH, Eh, and ligand concentration; and 3) the substrate surface, including the characteristics of porosity, abundance of specific components and their scavenging capacity and intensity (Tessier, et al, 1989).

Narrowing this discussion, bioavailability and mobility depend primarily on four major factors: (1) salinity; (2) organic complexation; (3) redox parameters; and (4) pH. An increase in salinity may release metals from sediment due to intensive decomposition of organic matter, and competition from magnesium and calcium for adsorption sites. The presence of organic complexes, especially synthetic chelators, may also remobilize metals. Changes in redox parameters affect the metal storage capacity in sediment. Anoxic layers in sediment tend to stabilize metal concentrations in sediment and porewater; aeration, through mixing, drying or resuspension, liberates metals (Forstner and Salomons, 1984). Acidification is one of the most common releases of metals in sediment. An decrease in acidity has a two-fold effect on metal movement; lower pH dissolves carbonates, releasing carbonate-associated metals, and acidic conditions with increased concentrations of H^+ ions compete with metals for binding sites (Forstner, et al., 1980). Aqueous environments however, are dynamic systems and little is understood

about how the above functions control the scavenging of trace metals by sediments or their subsequent release to the overlying waters (Tessier, et al, 1989).

SEDIMENT – TRACE METAL INTERACTIONS

A major control in metal dispersion is the *reaction site.* Reaction sites are the components present, organic or inorganic, within the sediment. These include: 1) iron oxides; 2) manganese oxides; 3) silica and aluminium oxides; 4) organic matter; 5) carbonates; and 6) secondary sulphides. The sediment components are intertwined and their influence on metal dispersion depends upon *capacity*, or their quantity and *intensity*, or their chemical activity. For example, per unit weight, iron in the form of an amorphous hydroxide gel will more effectively scavenge metals than iron present as crystalline Fe-oxides (Chao, 1984).

Within soils and sediment, there are a variety of processes that bond metals to sediment fractions (Chao, 1984, Gibbs, 1973). These adhering mechanisms include: 1) adsorption – desorption, (physical and chemical adsorption); 2) precipitation and solubilization; 3) incorporation within the crystal structure of minerals; and 4) biological mobilisation (complexation and chelation) and immobilisation.

Adsorption is one of the dominant reversible bonding processes in oxic sediments. Simply stated, adsorption is the accumulation of a substance at a solid interface without the development of a three dimensional molecular arrangement. Both physical and chemical adsorption results from electrostatic attraction and repulsion between negative electrons and the positive nucleus.

Physical adsorption is a long range interaction or "outer-sphere" interaction at the sediment-water interface occurring by electrostatic attraction involving permanent dipole

interaction or polarization involving induced dipole interaction. In a polar solvent like water, electrostatic interactions dominate. Since most natural particles tend to be charged at near neutral pH, physical adsorption is favoured for cations.

Chemical adsorption is stronger than physical adsorption and involves a short range or "inner sphere" interaction between trace metals and solids. Chemical adsorption may occur by competitive surface complex formation (or metal surface complexation) and ternary surface complexation. Chemical adsorption leads to the development of formal charges and long range affects, directly affecting the physical adsorption of other species (Lebeuf, 1992, Charlet, 1994).

Cation exchange capacity (CEC) is the capacity of a material to act as an ion exchanger; cation exchanger is a material with a large surface area (clay minerals, fresh Fe oxides, and organic material) that sorbs cations from solution and releases an equivalent amount of other cations into solution. It is based on the sorptive properties of negatively charged ionic sites (SIOH-, $AlOH_2$-, AlOH groups in clay minerals, $Fe(OH)_2$ groups in iron hydroxides, and carboxyl and phenolic OH groups in OM) towards positive charged cations. The balance between negative charges in the structure is selective and this accounts for preferential adsorption of specific cations. Among sediment fractions, a generalised sorbing sequence has been established: MnO_x > humic acids > Fe-oxides > clay minerals (Forstner, et al., 1980).

Clay-sized aluminosilicates are important reaction sites since their surface properties serve as a vehicle for other reaction sites. Sorption on clays is controlled by the number of free sorption sites on the clay surface. Free sorption sites are the product of free or broken bonding positions, and the proportion of atoms replaced with others

atoms of difference valences. Charge, pH, and hydration influence sorption as well as the type of clay that is sorbing. Heavy metals will sorb preferentially on clays that can expand to accommodate metals. Expandability enhances their exchange capacity and corresponds with the decrease in particle size and increase of the related surface area. Sorbing potential increases with cation exchange capacity in the increasing order of: montmorillonite > vermiculite > illite ≈ chlorite > kaolinite (Fergusson, 1990, Forstner, et al., 1980).

When a substance leaves a solution rapidly to form a micro-crystalline or amorphous solid, the substance is precipitating. If the nucleation is homogeneous, pure phase precipitation ensues. When a dissolved species is incorporated as a minor component into a solid phase that itself is precipitating, the dissolved species is co-precipitating. The introduction of foreign particles into the nucleation reaction is heterogeneous precipitation. Precipitation and co-precipitation of hydroxides, carbonates, and sulphides results when the solubility product (K_{sp}) is exceeded. It is impossible in some circumstances to clearly distinguish between adsorption and precipitation and often researchers have chosen to use the term adsorption and sorption to include both (Drever, 1988).

Surface precipitation is the growth of a solid solution on the surface of a solid phase. Foreign species in the hydrated layer of the solid may promote new material to grow as a solid solution rather than as a pure solid. Surface precipitation is the most common type of precipitation; solid solutions are likely to form in a variety of solid substrates.

There is an abundance of data collected from simple experimental systems involving heavy metal precipitation/dissolution, but this data is merely a guide in the complex world of natural aquatic systems (Forstner, et al., 1981). Most metals are undersaturated with respect to solid phases in oxic, near-neutral pH freshwater systems. Most river sediment has pH values between 7 – 8 and are oxygenated

Metals incorporated within a crystal lattice of minerals formed at higher pressure and temperature regimes (with the exception of carbonates) are essentially geological inert at surface conditions. Silicates comparatively have low to very low heavy metal contents. Pb is found in minerals where large monovalent or divalent metals occur (e.g. Pb may substitute for K^+ in muscovite and K-feldspars). Zn may be preferentially incorporated into silicates and oxides displacing iron and magnesium in minerals such as biotite and amphibole. Cu is magmatically partitioned into the early magmatic differentiates (e.g. olivine, pyroxene). A study of contaminated sediments (Hirst, 1962) found that Cr, V, Cu, Pb and lesser amounts of Co and Ni may structurally combine in the structures of degraded clay minerals (Cr and Cu in illite, and V, Co, Ni in montmorillonite).

Organic matter (OM) can affect the solubility, transport and distribution of trace metals by sorption, flocculation, and complexation. OM may sorb metals weakly by physical adsorption due to negative charges of organic colloids or form strong bonds by forming a complex with the metal or binding it through chelation. A quick perusal through the literature suggests that the sorption process between metals and organic matter is poorly understood. However, Jonasson (1972) described a preferential sorbing order for trace metals onto humic and fulvic acids: $Cu^{2+} > Pb^{2+} > Zn^{2+}$ > and Ni^2. Up to

1/3rd of the positions available for metal bonding in humic acids may be attributed to cation exchange capacity; the remaining 2/3^{rds} of the available positions exist as complexation sites (Rashid, 1971).

The scavenging ability of OM is attributed chiefly to functional groups within humic acids. Carboxylic acid (-COOH) and to a lesser extent phenol (-OH), and amino ($-NH_2$) functional groups complex with metals. Dissolved and particulate OM forms complexes (species of 2 or more simpler species) functioning as multidentate ligands for transitional metals. A multidentate ligand has more than one site available to bond with a metal. Complexes that involve multidentate ligands are chelates (a chelator is a ligand that binds to a metal through more than one atom); these are much more stable than unidentate ligands and the more complexing groups there are on a multidentate ligand, the more stable the complex. Complex stabilities for metals range widely in the literature, in part owing to the various mechanisms used to bind metals and the wide range of possible structures of organic matter. Stabilities of many complexes are susceptible to pH changes (Drever, 1988).

Sediment Components

Iron and Manganese Oxides

Iron and manganese oxides, hydroxides and oxyhydroxides, occur in a multitude of mineralogical forms resulting from the chemical weathering of minerals containing Fe and Mn and anthropogenic loading. They play a key role in chemical reactivity in soils and sediment within the secondary weathering environment (Oades, 1963). Fe/Mn oxides are ubiquitous in most freshwater environments and are strong metal scavengers. Of all the solid phases that comprise sediment, these oxides exert a tremendous

physiochemical influence on other minerals species and organic material that is all out of proportion to their concentration (Jenne, 1968).

Fe and Mn form mixed oxides owing to their similar chemical properties and ionic radii. They exist as nodules, cements, concretions, coatings and discrete particles of colloidal dimensions. Crystal structures of Fe/Mn oxides range from highly crystalline through cryptocrystalline to amorphous (Schwertmann, 1973). Usually what is referred to as hydrous Fe oxides implies a poorly crystalline form of FeOOH (Forstner, et al., 1981). In some sequential extractions, amorphous forms of Fe oxides or "active' forms, ($Fe(OH)_3.nH_2O$) have a separate step in the selective extraction scheme owing to their chemically reactive state. The amorphous forms exhibit higher specific surface area per unit weight than the more crystalline forms. The amorphous forms age by dehydration allowing for molecular re-arrangement in an increasing stable crystal form. The order of metal uptake may change to reflect changes in the internal ordering of the iron hydroxides.

Mn oxides have a higher scavenging ability for heavy metals than iron oxides on an equivalent weight basis (Chao, 1976). Mn oxides precipitate less rapidly than Fe oxides, but isomorphic substitution and penetration by foreign ions into extremely complex Mn oxide structures is much more extensive than in Fe oxides (Hall, et al., 1996).

Scavenging of metals may occur by any of the following mechanisms: adsorption (surface complex formation, ion exchange), co-precipitation, and penetration of the lattice (Chao and Theobald, 1976). Secondary hydrous Fe/ Mn oxides possess high adsorption capacities and will dissolve as redox potential decreases and reprecipitate as

the system becomes oxygenated. Alternating sequences of dissolution and precipitation keeps oxides in a highly active amorphous state facilitating the nonstoichiometric incorporation of foreign elements, especially metals. Metal incorporation depends upon the prevailing physicochemical conditions such as existing pH-Eh values, abundance, presence of organic material and other factors that are too numerous to generalise (Hall, et al., 1996).

Jenne (1968) indicated that in hydroxides containing metals, a minimum soluble value lies within the pH range of 9 –12. When pH was lowered, a marked increase in metal solubility was noted At pH 4, complete dissolution was achieved, and below pH 2, there is no adsorption of metals (Drever, 1988). Metals associated with Fe/Mn oxides are more strongly bound than in the exchangeable or carbonate phase of sediment (Davis and Leckie, 1978). Accumulations of metals with this sediment phase may not have an immediate biological impact, but a significant drop in pH may release metals into the water (Florence and Bailey, 1980).

Though studies on the behaviour of Fe and Mn in aquatic sediments is extensive in the literature (Jenne 1968, Chao et al., 1976, Tessier et al., 1980, Tessier et al., 1985, Slavek et al., 1985,) understanding of their physicochemical properties and modelling of trace metal partitioning has been severely limited due to the difficulties in separating Fe and Mn oxyhydroxides from the medium they occur in. The low concentrations, 0.1-3.0% dry weight, in the sediment matrix also hinders their study (Belzile, *et al.*, 1989).

Silica and Aluminium Oxides

Al and Si oxides do not possess the adsorptive capacities to the extent present in other sediment phases; their role as a geochemical control has not been adequately evaluated due to the lack of selective reagents (Chao, 1984).

Organic Matter

Organic material (OM) consists of primarily of C,H,O,N, and S that may be of biological or inorganic origin. OM may determine solubility, transport and enrichment of trace metals (Gruner, 1922) by forming organic-metallic complexes. When metals bond with organic ligands, the reactions tend to be non-reversible. However, if OM is < 5%, the metal-organic matter associated is less pertinent than other controls in the sediment, especially Fe-Mn oxides (Wilhem et al., 1979).

Organic matter, biologically or synthetically produced, includes a wide range of compounds but trace metal studies have primarily concentrated on the role of humic acids and fulvic acids because of their ubiquitous occurrence and quantity. Fulvic acids are characterised by low molecular mass, larger functional groups, and greater solubility that allows them to transport trace metals whereas humic acids retain metals due to their sheer abundance (Jenne, 1976).

Metals associated with organic matter are relatively strongly bound; they are unlikely to be bioavailable (Morrison, 1987) except where this fraction behaves as a transport mechanism and sink for metals like Cu and Pb, both of which possess high stability constants with organic compounds (Mantoura et al. 1979). Complexation preference is given to divalent ions opposed to monovalent ions with an affinity series order of Pb > Cu > Ni > Co > Zn > Mn > Ba > Cu > Mg.

Carbonates

Carbonates in sediment usually consisted of calcite and aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, and magnesite ($MgCO_3$). Metals bond to carbonates by adsorption and precipitation/co-precipitation by organic or inorganic processes. Metals may be encouraged to form insoluble metal hydroxides through the capacity of carbonates to increase pH and hydrolyse metal ions (Chao, 1984). As a source of trace elements, carbonates contain very low concentrations (Turekian, et al., 1961) with the rare exception of select trace metals such as Zn and Cd (Forsnter, et al., 1981).

Secondary Sulphides

Sulphides occur as a result of reactions between metals and sulphide ions in a reducing environment. Since all samples were collected in an oxidizing environment, secondary sulphides may only play a minor role in controlling metal speciation in this study.

SELECTIVE EXTRACTION OF METALS

Sequential extraction is a selective dissolution technique designed to partition metals from various fractions in the sediment by subjecting one aliquot to a progressively stronger series of different reagents. The technique is based on the knowledge that elements partition into chemical forms in relationship to solid phases in the sediment. Speciation studies have sought to elucidate the mode of element occurrence, enhance geochemical contrasts between mineralised and non-mineralised zones, and to determine lithological and anthropogenic effects.

Early sequential extractions were initially designed to determine metal partitioning in soils (Le Riche et al., 1963) but were quickly refined and adapted to

exploration studies in sediment geochemistry (Rose et al., 1971, Chao et al., 1976, Hoffman et al., 1979. Filipek et al., 1981). Interest in selective extractions spilled into other disciplinary areas of the geosciences, mainly to determine the mode of occurrence of a trace metals in marine (Gupta et al., 1975, Forstner, et al., 1981), river and lake sediment (Gibbs, 1977, Tessier et al., 1979, Tessier et al., 1980, Bendell-Young, et al., 1992). Such studies inherently lend themselves to environmental assessment.

Sequential extractions estimate the quantity of metals partitioning among different sediment fractions. It is generally accepted that metals occurring as a dissolved species or adhered to particle surfaces by adsorption, are readily bioavailable (Morrison et al. 1984a, Morrison et al. 1984b. Tessier et al. 1984, and Bendell-Young, 1991). If the metal is bound in organic or metal hydroxides, the metal is not as easily available to the biota. Metals incorporated within a residual mineral structure are considered unavailable to living organisms (Gibbs, 1973, Chao, 1984).

Reagents employed in extraction process can be divided into the following categories based on their chemical behaviour: *concentrated inert electrolytes* [desorb electrostatically held (or absorbed) metals]; *weak acids* [dissolve carbonates, desorb specifically held (adsorbed) metals]; *reducing agents* [reduce Fe/Mn oxyhydroxides]; *complexing agents* [compete for metals complexed with organic material, dissolve precipitates]; *oxidizing agents* [oxidize organic material and sulphides]; and *strong mineral acids* [dissolve resistant oxides, sulphides, and aluminosilicates].

Selectivity at each step in the procedure is not 100%. The selectivity depends upon factors such as the choice of reagents used, the sequence the reagents are applied, time and nature of contact between the sediment and reagent, and sample to volume

ratios. The grain-size of material examined will also affect the reaction; the finer the sediment particles, the more surface area exposed to the reagent.

One of the most commonly used procedures in 'environmental' sediment geochemistry is that of Tessier et al. (1979, 1989) and derivations thereof (refer to Campbell, et al. (1988) for review). Tessier's extraction (1979, 1989) extracts metals from six components in the sediment, namely: (1) 'exchangeables' which includes clays, hydrated oxides of Fe and Mn, and humic acids participating in the adsorption of trace metals; (2) carbonates, (susceptible to pH changes); (3) Mn oxides & (4) Fe oxides, existing as nodules, concretions, cement or coatings (oxides scavenge trace metals and are thermodynamically unstable in anoxic environments); (5) organic matter, (trace metals bound with organic matter, living organisms, etc.); and (6) residual metals (or metals locked into the silicate structures). Metals incorporated in mineral structures are not expected to be released into solution (Tessier, et al., 1979).

In this study, metals were extracted in three forms, namely: adsorbed, exchangeable and carbonate associated metals (referred to as the AEC step throughout the rest of the thesis); metals complexed or chelated with the organic fraction of the sediment (referred to as the Organic step throughout the thesis) ; and metals bound with Fe/Mn oxyhydroxides (referred to as the Reducible step throughout the thesis). In the sequential extraction literature, trace metal partitioning is commonly referenced to a certain sediment fraction, but it is more correctly related to how the metal is bonded to the sediment that sequential extraction partitions. It is therefore only for convenience that the metals will be discussed in the context of AEC, Organic and Reducible sediment fractions throughout the thesis.

CHAPTER 4

METHODS OF INVESTIGATION

SEDIMENT SAMPLING AND FIELD MEASUREMENTS

Sediment was collected from the Detroit River bottom and Lake St. Clair substrate with a stainless steel Petit Ponar™ grab sampler during the spring and fall of 1996. Three to five kilograms of sediment was taken from each site to ensure that each site produced at least 5 g of the < 63 μm grain-size fraction sought for geochemical analysis. In order to normalise trace metal concentrations with respect to grain-size, only the < 63 μm fraction of sediment was collected from each site for geochemical analysis. The < 63 μm grain-size fraction includes silt and clay-sized particles. The sediment was transferred from the ponar into an acid-washed container where it was homogenised and then wet-sieved with a 63μm nylon mesh with 'lake' or 'river' water ('lake' or 'river' water would inhibit the loss of exchangeable metals. The < 63 μm sediment fraction was transferred into acid-washed sealable plastic bags and iced until transport to the laboratory freezer. The samples were frozen to inhibit biological activity and prevent further chemical transformation (i.e. change in metal species in sediment and/or change in phase association) in the sediment. A bulk sediment sample was also collected from each site for grain-size analysis to determine the percentage of the < 63 μm sediment fraction.

Each site was selected to ensure uniform coverage of the study area and to avoid areas of obvious disturbance to the substrate (i.e., the dredged shipping channels). Sampling was also influenced by the distribution of fine-grained material. The location of each site was recorded with a Garmin™ GPS 4 5XL personal navigator. Site location,

sediment description, weather conditions, water depth, sediment pH, dissolved oxygen, Eh, and temperature were also measured when possible (Chapter 5).

ANALYTICAL METHODS

GEOCHEMISTRY

Trace metal (Pb, Zn, Ni, Cu and Cr) and major element (Ca, Mg, Fe and Mn) concentrations were determined with a sequential extraction procedure. Major and other element (Si, Fe, Al, Mg, Ca, Mn, K, Na, Ti and P) total concentrations were determined after a lithium metaborate-tetraborate fusion. The < 63 μm grain-size fraction was used in both analyses.

Sequential Analysis

The procedure used for the sequential analysis was a three step adaptation compiled from various sources (Tessier et al., (1979), Hall et al., (1996*a*), Hall et al., (1996*b*). The first step releases metals that are non-specifically adsorbed, exchangeable or associated with carbonates (the AEC step) with a sodium acetate solution (NaOAc) as previously described by Jackson (1958), Le Riche et al., (1977), Grossman et al., (1961), Tessier et al., (1979), Banin et al., (1995), and Hall et al., (1996*b*). A sodium actetate buffer solution removes metals associated with carbonates by dissolving the carbonates and releases exchangeable metals held on clays, organic matter and Fe/Mn oxyhydroxides by replacing the exchangeable metals with Na^+.

The second step of the extraction utilised a solution of sodium pyrophosphate ($Na_4P_2O_7$) an alkaline complexing agent, to liberate metals associated with organic matter in the sediment. Alkali pyrophosphates has been used extensively in the soil

sciences to remove organic-chelated metals (McKeague, 1967, Bascomb, 1968, Tan, 1978) and has become routine in sequential extractions (Chao et al., 1976, Learned et al., 1981, Hall et al., 1996*b*). Sodium pyrophosphate removes metals bound with organic matter by removing the stabilising cations (Ca, Al, Fe, etc) within the organic matter by precipitation or the formation of chelates or co-ordination complexes with the pyrophosphate ion.

The final step of the extraction leached metals associated with iron and manganese oxyhydroxides. A strong reducing solution of hydroxylamine hydrochloride ($NH_2OH.HCL$) adopted from previous work by Chester et al., (1967), Chao et al., (1972), Bogle et al., (1981), Chao et al., (1983), Kersten et al., (1989), Hall et al., (1996*a*), Hall et al., (1996*c*), was selected. Acidified hydroxylamine hydrochloride reduces Fe and Mn to their ferrous and manganous forms and keep in solution relatively large amounts of metals liberated (Tessier et al., 1979). The sequential procedure outlined below was selected and modified to ensure the results of this thesis were comparable with other studies that utilised the same certified reference material.

Reagents

All reagents and acids were of analytical reagent or equivalent grade. Sodium acetate (BDH), sodium pyrophosphate (Sigma) and hydroxylamine hydrochloride (BDH) were purchased and used as received. The reagent solutions were made with de-ionised water. (This water will be referred to as MilliQ water throughout the thesis). All glass and plasticware used in the procedure was acid-washed in 13% nitric acid in double-distilled water prior to use. Nalgene™ polypropylene centrifuge tubes, 38 mL, and screw-on caps were used for the extraction.

Sample Preparation

The frozen sediment samples were removed from the freezer and thawed at 4°C, 24 hours prior to the extraction. Porewater was removed from the thawed sediment for analysis by centrifugation at 7 000 rpm for 15 minutes at room temperature. (Porewater was retained and analysed to see if post-depositional and diagenetic reactions affected metal distribution). The porewater was filtered from the sediment (using Whatman's #4 Qualitative filter paper) into an acid-washed polypropylene bottle. The weight of the porewater was recorded and it was acidified with 120 μL of concentrated HNO_3. The porewater was brought up to 30 mL solution with MilliQ water. The wet, de-watered sediment, was then subdivided into three sub-samples: a) a 0.5 g sample for the sequential extraction, b) a smear mount for XRD analysis to examine the initial mineralogical phases present in the untreated sample, and c) a sub-sample to determine remaining % water of the sediment.

Extraction Procedure

An overview of the sequential procedure is located in Appendix 1.

(1) Exchangeable, Adsorbed, Carbonate, and Water Soluble (AEC Step)

10 mL of 1 M NaOAc (adjusted to pH 5.0) was reacted with the 0.5 g dewatered sediment sample for six hours at room temperature with continuous agitation. Supernatant solution was filtered off and the sediment was rinsed twice with MilliQ water (this water was added to the analytical solution). This step was repeated under the same conditions.

(2) Bound to Organic Matter (Organic Step)

35 mL of 0.1 M $Na_4P_2O_7$ was added to the residue from Step (1). The residue reacted with the sodium pyrophosphate for 1 hour at room temperature with continuous agitation. The supernatant solution was drained off and procedure was repeated. Sediment was rinsed twice, (only after the second reaction with $Na_4P_2O_7$), with MilliQ water (added to the analytical solution).

(3) Associated with Fe-Mn Oxides (Reducible Step)

15 mL of 1.0 M $NH_2OH.HCL$ was added to the residue from Step (2). The residue reacted with the hydroxylamine hydrochloride solution in a heated waterbath (90°C) for three hours with occasional agitation. The supernatant solution was filtered off and sediment was rinsed twice with an HOAc solution (25% v/v MilliQ water and concentrated HOAc). The rinse solution was added to the analytical solution. This procedure was repeated as outlined above, except the second extraction was only 1.5 hours.

For selected samples, an experimental replicate was run through the entire extraction procedure to measure pH of the reagents following the reaction, and to collect sediment for smear mounts for XRD analysis to assess the effectiveness of the reagent by examining the residual mineralogy. By running a replicate sample, the initial sample was not contaminated by the intra-procedure sampling. pH measurement of the supernatant, were recorded prior to subsequent rinsing between each step. Smear mounts were made on glass slides for XRD analysis. Sediment was sampled from the replicate test-tube immediately after the supernatant was drained. The sediment was smeared evenly onto a glass slide with a clean spatula with a minute amount of vacuum grease to prevent the slide from powdering after drying.

In the absence of a certified sediment reference material (CRM) for sequential extractions, LKSD-4, a certified reference material comprised of composite centre lake sediment issued by the Canadian Certified Reference Material Program (CCRMP) (Lynch, 1990), and an internal laboratory standard collected from the western basin of Lake Erie, referred to as SEDA throughout this thesis, were used as reference materials in each batch of the sequential procedure. Analytical reproducibility of the extraction procedure was tested with SEDA and LKSD-4; precision results are reported in Chapter 5.

Concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) with an ARL Maxima model. The operating conditions are listed in Appendix 2. Calibration standards (prepared from Fisher analytical standards), blanks, samples, and reference material duplicates were run with each batch. Calibration blanks were matrix matched with the standards and made from stock solutions to minimise matrix effects, (matrix effect is the interference caused by the composition of the matrix in which the element to be analysed resides). Method blanks are listed in Appendix 3 in μg/g for the trace metals and Appendix 4 for the major elements. Determination limits, obtained by replicate determinations of reagent blanks, are listed in Appendix 5. The range of detection limits, (3σ of the background noise), are listed in Appendix 6.

Major Element Total Analysis

Thirteen samples of the < 63 μm grain-size sediment fraction were selected for major element analysis. Major elements (Si, Al, Fe, Mg, Ca, Mn, Na, K, Ti and P) were determined by bringing into solution a fusion of 0.5 g of wet sediment with a mixture of

lithium metaborate and lithium tetraborate that was subsequently dissolved with dilute nitric acid/EDTA/ and MilliQ water. Prior to fusion, the loss on ignition was obtained for each sample to determine the organic, volatile and carbonate components of the sediment. The procedure used was adapted from a fusion procedure used by the Geological Survey of Canada (Z.X. Chen, pers comm)

Procedure

Loss on Ignition (LOI) was determined prior to the fusion. Half a gram of wet sediment was measured into porcelain crucibles and ignited in a furnace at 900°C for 30 minutes. After 30 minutes, the samples were removed from the hot oven and placed in a desiccator to equilibrate to room temperature. After reaching room temperature, the crucible and ignited sediment was re-weighed to calculate the loss on ignition.

A lithium flux of 1.0 g of $LiBO_2$ (lithium metaborate, Sigma, ACS Reagent Grade) and 0.5 g $Li_2B_4O_7$ (lithium tetraborate, Sigma, 99% Titration Grade) were mixed thoroughly with 0.5 g of sediment in a pre-ignited graphite crucible. The sample was fused at 900°C for 30 minutes. After 30 minutes, the molten melt was quenched in acid-washed polypropylene beakers containing 150 mL MilliQ water, 10 ml of EDTA solution (made by dissolving 16 g of EDTA (ethylenediaminetetra-acetic acid, using Sigma "ACS Reagent") in 100 mL of MilliQ and 20 mL of NH_4OH) and 10 mL of concentrated HNO_3. The samples were stirred with a magnetic bar until dissolution was complete. The solution was transferred into a 250 ml polypropylene container by filtration through a dry #42 Whatman's filter.

Accuracy was verified by running a reference standard Syenite SY-4 and comparing study values with the certified values of SY-4. Precision was obtained by

running SY-4 (n=2) and LKSD-4 (n=5); LKSD-4 was added because it is a lake sediment composite reference material and is closer in composition to sediment than the syenite. Accuracy and precision results are listed with the data in Chapter 5. The concentrations were determined by an ARL Maxima model ICP-OES at the University of Windsor.

Carbon, Nitrogen, and Sulphur Analysis

Total carbon (TC) within an aqueous system, includes all forms of organic material such as live micro-organisms, suspended particles, dissolved molecules and all forms of inorganic carbon in the form of carbonates (Faure, 1991). Carbon, along with nitrogen and sulphur were determined in selected sediment samples by a CE Instrument EA-1110 Elemental Analyser at the University of Ottawa, Ottawa, Ontario. Samples were combusted by ' dynamic flash combustion' process at 1800°C. The resulting gases were separated in a packed column GC and measured on a TCD detector. The precision of this method for carbon, nitrogen and sulphur were reported to be ± 0.3%, 0.1% and 0.2%, respectively.

Grain-size Analysis

Bulk sediment samples were collected to determine the grain-size distribution at the sediment sample sites. Cobbles, and shell fragments were removed from the bulk sediment samples in order to prevent skewness in the grain size analysis. The remainder was sent to Uppsala University, Institute of Earth Sciences, Quaternary Geology in Uppsala, Sweden for grain-size analysis. The analysis was made with a Laser CILAS 715 granulometer. The reproducibility error, given as one standard deviation (calculated on five samples repeated three times), was reported as < 5% based on 100 g sub-samples.

Prior to analysis, all samples were sieved through a 200 μm mesh in order to remove shell fragments and avoid an anomalous bimodal distribution.

X-RAY DIFFRACTION

X-ray diffraction has been utilised in tandem with sequential extractions to identify minerals present prior to extractions and to evaluate the selectivity of various reagents with sediment, soil or other media. XRD has been used in Tessier et al. (1979), to evaluate the whole sediment and reagent selectivity in fluvial sediment. Tipping et al. (1985) employed XRD to examine selectivity of reagents with Fe/Mn oxides precipitated on the walls of a disused lead mine; and Han and Banin (1995) utilised XRD to study the selectivity and effectiveness of NaOAc-HOAC at varying pHs in carbonate-rich soils. Since the Lake Huron-Lake Erie corridor lies within Palaeozoic carbonates, XRD may be particularly useful in determining if the first step of the reaction removes all the carbonate.

Sample Preparation

A series of slides were prepared from residues of the sequential extraction. Samples for this study were selected to examine the sediment and mineralogical diversity within the substrate of the waterway and how the sediment reacted with the reagents in the sequential extraction. The sediment for each slide was scooped out of the replicate test-tube and smeared with a plastic spatula onto a clean glass slide with a drop of vacuum grease. Some of the initial slides powdered after air-drying and could not be x-rayed. To avoid this problem, the majority of the slides were prepared as a slurry with vacuum grease. Each sample generated 7 slides for study:

1) dewatered "untreated" sediment (porewater removed as described in the geochemical procedure); 2) dewatered sediment reacted with 0.1 M NaOAc (pH 5.0) for 6 hours at room temperature (AEC Step); 3) sediment from 2), reacted with 0.1 M NaOAc (pH 5.0) for 6 hours at room temperature (AEC Step); 4) sediment from 3), reacted with 0.1 M Na-pyrophosphate for 1 hour at room temperature (Organic Step); 5) sediment from 4), reacted with 0.1 M Na-pyrophosphate for 1 hour at room temperature (Organic Step); 6) sediment from 5) reacted with 1.0 M $NH_2OH.HCL$ for 3 hours at 90°C (Reducible Step)); 7) sediment from 6) reacted with 1.0 M $NH_2OH.HCL$ for 1.5 hours at 90°C (Reducible Step).

Slides were air-run at room temperature on a PW 1077 diffractometer at the Department of Earth Sciences at the University of Windsor. Each slide was scanned from 3°θ to 75°θ at a 0.02 step interval at a rate of 0.5° per minute at a 40 kV, 20 mA setting using CuKα radiation.

After the samples were run, the diffraction pattern was manipulated by Traces, a Sietronics XRD Trace Processing Software. Diffraction patterns were shifted to cover any machine angle error. Diffraction peaks were manually selected and background radiation was manually subtracted. The diffraction pattern was smoothed by a 5 point running average. Mineral identification was aided by a micro Powder Diffraction Search/ Match computer program written by Fein-Marquart Associates, Inc., based on the Powder Diffraction Files, Sets 1 to 4 (Mineral Subfield), Joint Commission on Powder Diffraction Standards, International Centre for Diffraction Data.

CHAPTER 5

RESULTS

SEDIMENT CHARACTERIZATION

LAKE ST. CLAIR AND ST. CLAIR DELTA SEDIMENT

Table 2 lists the field observations recorded at each sample site in the study area.

Table 2. Field Measurements from Walpole Island and Lake St. Clair Sediment.

Site	Location	Date	Temp of Water °C	Water Depth (m)	pH
WI-4	N 42°35'56" W 82°31'56"	May 3/1996	11.5	1.5	6.85
WI-5	N 42°38'02" W 82°30'00"	May 3/1996	9.7	0.5	7.06
LS08	N 42° 20'59" W 82° 49'58"	Oct 1/96	N/A	4.0	N/A
LS09	N 42° 21'00" W 84° 44'58"	Oct 1/96	15.5	5.2	7.77
LS10	N 42° 20'59" W 82° 39'58"	Oct 1/96	15.0	5.2	7.58
LS16	N 42° 26'30" W 82° 40'29"	Oct 26/96	12.8	6.3	7.87
LS17	N 42° 26'06" W 82° 45'10"	Oct 26/96	N/A	5.7	N/A
LS18	N 42° 26'02" W 82° 50'44"	Oct 1/96	16.1	4.7	7.67
LS19	N 42° 30'59" W 82° 50'25"	Oct 26/96	13.3	4.0	8.34
LS20	N 42° 30'19" W 82° 45'18"	Oct 26/96	13.2	5.5	7.93
LS21	N 42° 30'22" W 82° 40'40"	Oct 26/96	12.7	4	7.9
LS24	N 42° 20'40" W 82° 54'58"	Oct 1/96	16.0	4	6.74

Samples WI-4 and WI-5 were collected from channels of the St. Clair Delta during the spring of 1996. WI-4 was collected from the substrate of the clear, swift-flowing waters of the Chematogen Channel separating Walpole and Squirrel Islands (Figure 2). The Chematogen Channel is a shallow (1.5 m in depth), marsh-lined strait. Channel sediment consisted of well-sorted silt and sand, light brown in colour and

containing virtually no organic matter. Sample WI-5 was collected from Chenal Ecarte, 500 m east of the offshoot of the channel from the St. Clair River proper (Figure 2). The sample was collected 0.5 m below the turbid waters of the channel. The substrate was sandy with minor silt and clay, bound by abundant root matter.

Well-sorted quartz sand was collected at site LS21, nearest to the St. Clair Delta. The sand-sized particles were brown-beige to grey. East of the delta and north of the dredged shipping route, the lake bottom was semi-consolidated and silty littered with shell fragments and organic material. At sites LS17 and LS16, near the lake centre, sediment was semi-gelatinous and silty to muddy. At LS16, abundant shell fragments were noted in the grey-brown mud. The sediment at LS17 was faintly laminated with reddish-brown silt-sized particles at the top of the sediment-water interface. Sites LS17 and LS16 mark the deepest part of the lake.

Along the lake's south shore, sediment scooped up at sites LS09 and LS10 consisted of silty and clay-sized particles. The sediment was also semi-consolidated, brown, and contained shell fragments. Many of the grab samples along this transect were filled with cobbles and pebbles which were removed from the samples, including LS08. The sediment at site LS08 was choked with zebra shell fragments up to 2 cm in length. At site LS24, near to the Detroit River, sediment was semi-consolidated with very dark brown to blackish silt laminations.

Along Lake St. Clair's eastern shore, the sediment at LS18 was composed of semi-consolidated clays and silts, but northward the lake bottom became sandy and non-consolidated with shell fragments up to 4 cm and lacustrine grasses. A grey silty layer marked the surface of the sediment-water interface at LS19.

The pH values ranged from 6.74 (LS24) to 8.34 (LS19). Delta sediment pH of the porewater averaged 6.96 whereas the average pH of the lake sediment was slightly more alkaline at 7.73. Calibration errors hindered Eh readings.

Detroit River Sediment

Table 3 lists the field data collected at the sample locations from the Detroit River substrate.

Table 3. Field Measurements from Detroit River Sediment.

Site	Location	Date	Temp of Sediment °C	Water Depth (m)	pH	DO %
DT28	N 42°18'30" W 83°04'30"	April/96	7.09	1	9.4	4
DT29	N 42°18'45" W 83°04'45"	April/96 11:00	8.80	1	6.95	7.0
DT30	N 42°15'00" W 83°06'40"	April/96	8.8	1.5	7.19	9.0
DT31	N 42°16'40" W 83°06'30"	April/96	9.0	1	7.0	7.34
DT32	N 42°10'51" W 83°07'00"	April/96	12.7	1	7.02	7.0
DT33	N 42°05'45" W 83°07'30"	April/96	10.6	2	7.02	8
DT34	N 42°10'51" W 83°07'58"	April/96	14.0	1	7.33	36

Downstream from Lake St. Clair, the first sediment sample was collected along the Windsor waterfront south of Belle Isle (DT28). Further downstream, DT29 was collected on the Canadian site under the Ambassador bridge. At both locations, sediment was comprised of well-sorted, brown-black silts and clays. At DT30, south of where the Rouge River drains into the Detroit River, sediment consisted of unconsolidated light-brown silts and clays with abundant zebra mussel shells. East of Zug Island at site DT31, sediment was primarily clay and silt-sized and blackish-brown in colour. The sediment had a sticky quality and possessed a strong oily odour. At

DT34, collected south of Fighting Island, sediment was light brown to grey and consisted of clay and silt-sized particles with abundant Zebra shell fragments. At site DT32, adjacent to Turkey Island, the riverbed was semi-consolidated and contained blackish clay-sized particles and abundant weeds. At site DT33, the last sample collected downstream near the Bois Blanc Island , the sediment consisting of well-sorted, semi-consolidated silt and mud with shell fragments and a blackish residue (oil/tar-like substance). During the sample preparation in the lab, it was noticed that Detroit River sediment contained minute quantities of magnetic metal filings. Sediment porewater pH ranged over a short distance from 6.95 (DT29) to 9.4 (DT28) with an average pH value of 7.42 downstream

GRAIN-SIZE DISTRIBUTION

The raw grain size data is listed in Appendix 7. Particle size distribution of the bulk sediment samples are given Table 4 showing the division between sand, silt and clay-sized particles and percent of the < 63 μm fraction at each site. The grain size data does not include shell fragments and cobble-sized particles. These were removed prior to analysis.

Table 4. Particle Size Distribution of Sediment Collected from Walpole Island, Lake St. Clair and the Detroit River. (The percent < 63 μm is the sum of the silt and clay-sized particles).

Sample	% Sand	% Silt	% Clay	% < 63 μm
WI-5	54	9	37	46
LS21	83	3	14	17
LS20	15	32	53	85
LS19	36	15	49	64
LS16	33	29	39	68
LS17	3	16	81	97
LS18	18	20	62	82
LS10	21	6	72	78
LS09	13	20	67	87
LS08	45	5	51	56
LS24	37	5	58	63
DT28	44	6	50	56
DT29	2	7	91	98
DT30	14	9	77	86
DT31	10	9	82	91
DT32	14	15	71	86
DT33	19	7	74	81

The samples collected from the delta (WI-5) and proximal on the lakeside of the delta (LS21, LS16) have the coarsest grain-size fraction as expected as it is a high energy environment where the winnowing of finer-grained material leaves sandier substrates. A sandy substrate was encountered along the eastern shoreline (LS19) and along the channelway to the Detroit River (LS08, LS24). At site LS17, near the lake centre, 97% of the sediment is silt and clay-sized. The thickest accumulation of recent silt and clay occur near the centre of the lake, measuring from 30 to 35 cm in thickness (Mudroch and Hill, 1975, Thomas et al., 1976, Rossmann, 1988). The Detroit River had a higher proportion of silt and clay, averaging around 83%, than sand except for DT28 (44% sand).

GEOCHEMICAL RESULTS

The precision results are presented in two sections; the first section covers the sequential precision data and sample results and the following section covers the total major element precision data and sample results.

SEQUENTIAL EXTRACTION

Trace metal concentrations are listed in Table 7 and major element concentrations are listed in Table 8. Porewater concentrations were not included since the concentrations were low or below detection limits. Concentrations of arsenic, antimony and mercury, though determined, were not compiled for the thesis since the values were sporadic and often below detection limits.

Trace Metal Analytical Precision

Precision of the sequential extraction procedure was determined by using LKSD-4, a certified reference material (CRM) issued from CCRMP and the in-laboratory standard of Lake Erie sediment, SEDA. LKSD-4 was selected for this project since there is previously published research in total, partial and sequential extractions using this CRM (Lynch, 1990, Hall et. al., 1996*a*, Hall et. al., 1996*b*, Hall et. al., 1996*c*. Table 5 presents the mean, standard deviation and relative standard deviation of the trace metal concentrations for the 7 samples of SEDA and the 10 samples of LKSD run during this study and compares these values with other published LKSD-4 data. A complete listing of SEDA and LKSD-4 trace metal concentrations are listed in Appendix 8.

Hall et al. (1996a) used LKSD-4 as one of a series of CRM tests with a sequential extraction procedure. Though the AEC step in Hall's study was leached with an ammonium acetate reagent versus the sodium acetate reagent used in this study, the AEC

values are still comparable. The sum of the three fractions in this study can be compared with values published by Lynch (1990). Lynch's LKSD-4 element concentrations were obtained by a partial extraction employing a dilute HNO_3- dilute HCl technique and was analysed by ICP-OES and AAS; Lynch's values were not certified but provisional at the time of publication.

Table 5. Precision results of trace metal data obtained from the sequential extraction.
Mean (μg/g), standard deviation (μg/g) and relative standard deviation (%)
for elements in the three phases of the extraction for SEDA and LKSD reference materials

	Phase			
	AEC Step	Organic Step	Reducible Step	Total
Pb-SEDA	51± 3, 5%	46± 3, 6%	42± 5, 13%	137± 9, 7%
Pb-LKSD	46± 4, 9% 43.9± 0.67 Hall[1]	29± 4, 14%	21± 3, 15%	95± 7, 7% 91± 6 Lynch[2]
Zn-SEDA	98± 5, 5%	191± 24, 13%	195± 18, 9%	485± 46, 10%
Zn-LKSD	54± 18, 33% 68.1± 1* Hall[1]	43± 29, 67%	75± 22, 29%	168± 13, 8% 195± 6 Lynch[2]
Ni-SEDA	16± 2, 15%	50± 2, 4%	47± 4, 9%	117± 7, 6%
Ni-LKSD	4± 1, 18% 4.85± 0.11 Hall[1]	4± 1, 24%	15± 2, 11%	22± 1, 7% 31± 4 Lynch[3]
Cr-SEDA	8± 0.32, 4%	55± 3, 5%	74± 7, 10%	141± 6, 5%
Cr-LKSD	1± 0.3, 37% 0.89± 1.4 Hall[1]	BD 1± 0.3, 37%	7± 1, 22%	7± 1, 19%
Cu-SEDA	22± 3, 12%	53± 3, 6%	51± 6, 12%	129± 11, 8%
Cu-LKSD	2, <0.5 Hall[1]	5± 1, 19%	9± 2, 22%	13± 4, 34% 31± 4 Lynch[3]

*Zn was analysed by FAAS in this study.
[1] AEC values from Hall et al., (1996*a*).
[2] Total values from Lynch (1990)

SEDA Precision

Reproducibility of results from the first step of the sequential extraction are excellent for SEDA; precision of the trace metal values, except for Ni (15% RSD), are under 10 % RSD. Considering the rudimentary approach this project has taken, relative standard deviations as a gauge of precision below 15% is acceptable. In general, RSD's

at and below 10% are be considered excellent (Vander Voet, 1993). In the organic step of the extraction, the SEDA RSD values range from 4 to 13. In the reducible step of the extraction, SEDA RSD's range from 9 to 13%.

LKSD-4 Precision

Reproducibility of the extraction effectiveness of trace metals in LKSD-4 exhibit a wider range of variation. RSD values for Cr (37%) and Ni (18%) as measurement of deviation is high, but it is important to note that the actual concentrations are low; the LKSD-4 Cr average is 1 $\pm$0.3 ppm, and Ni is 4 $\pm$1 ppm. This effect is also present in the steps when concentrations hover just above the detection limit. Precision of Zn reproducibility appears to be problematic.

LKSD-4 concentrations from Hall et al. (1996) for the AEC step are within the standard deviation results from this study. The LKSD-4 element concentrations from Lynch's study are not in close agreement with the values obtained in this study but it should be stressed Lynch used an aggressive partial extraction which may have liberated more metal than the sum of the sequential extraction steps employed in this study.

Major Element Analytical Precision

Table 6 presents the mean, standard deviation and relative standard deviation for Mg, Ca, Mn and Fe concentrations for the 7 samples of SEDA run and the 11 samples of LKSD-4 run in this study and compares these values with previously published LKSD-4 concentrations. A complete listing of SEDA and LKSD-4 Mg, Ca, Fe and Mn concentrations are listed in Appendix 9. Previously published data on LKSD-4, as previously outlined with trace metal precision, allows for comparisons between major element LKSD-4 concentrations in this and other studies.

Table 6. Precision of Major Element Data Obtained from Sequential Extraction
Mean (μg/g)1, standard deviation (μg/g)1 and relative standard deviation (%)
for elements in the three phases of the extraction for SEDA and LKSD controls.

	Phase			
	AEC	Or	Red	Total
Mg-SEDA	8648±599 (7%)	16378±1177 (7%)	15722±1895 (12%)	41409±1785 (4%)
Mg-LKSD	537±31 (6%)	20±10 (48%)	2078±390 (19%)	2663±396 (15%)
Ca-SEDA	18446±1292 (7%)	21330±1144 (5%)	20335±2285 (11%)	61404±2245 (4%)
Ca-LKSD	7150±507 (7%)	532±110 (21%)	658±87 (13%)	8245±383 (5%)
	6800±440 Hall[1]			
Mn-SEDA	305±22 (7%)	329±18 (6%)	314±35 (11%)	973±26 (3%)
Mn-LKSD	274±21 (8%)	25±3 (13%)	112±17 (15%)	407±24 (6%)
	223±2 Hall[1]	239 Hall[2]		420±9 Lynch[2]
Fe-SEDA	2002±138 (7%)	27600±2403 (9%)	26447±3365 (13%)	57281±4686 (8%)
Fe-LKSD	267±26 (10%)	3136±216 (7%)	10913±2241 (21%)	14306±2449 (17%)
	260±0 Hall[1]	3619 Hall[2]		26000±3000 Lynch[2]

[1] AEC values from Hall et al., (1996*a*).
[2] Total values from Lynch (1990)

SEDA Precision

The precision obtained from replicates of SEDA were excellent for the procedure; all the values were below 13% RSD. In the first step of the sequential extraction, SEDA RSD values for the four major elements is 7 %. RSD values for the second step of the extraction range from 5 to 9 %. In the final step of the sequential extraction, RSD values range from 11 to 13 %.

LKSD-4 Precision

LKSD-4 reproducibility for the first step of the sequential extraction is excellent for LKSD-4; all the major element values are between 7 and 10 % RSD. In the organic step of the extraction, the LKSD-4 RSD values range widely from 5 to 48%. Only Mn and Fe RSD's are below 15%. The relative standard deviation for magnesium is 48%, but it should be noted that the concentrations are near the detection limits. Calcium

however, has relatively higher concentrations, but still has a wide margin of relative standard error. In the reducible step of the extraction, RSD's for LKSD-4 range from 13 to 21% for Ca and Mn but Mg and Fe variance exceeds 15 % RDS.

The AEC comparisons between LKSD-4 concentrations extracted in this study and Hall et al., (1196a) are agreeable. The calcium mean obtained for this study and from Hall et al., (1996*a*) lie within each other's standard error. The mean Mn concentration is slightly higher than the Mn mean reported in Hall et al., (1996*a*). Hall's average Fe concentration is within range of the standard deviation obtained for Fe in this study.

Comparing partial extraction totals for LKSD-4, Lynch's total for Mn is within the standard error of the value obtained from this study. Fe totals from this study are well below the concentration that Lynch extracted. Since Lynch did use a more aggressive extraction procedure, it is expected that Lynch would extract higher concentrations of the major elements that the concentrations extracted from the sequential procedure employed in this study.

Distribution and Concentration

Trace metal and major element concentration and partitioning are presented in stacked bar graph diagrams (Figures 6 – 10). The bar graph diagrams are an illustrative form of concentration and partitioning among the three steps of the sequential extraction data listed in Table 7 and Table 8. The top bar graph of each diagram shows the distribution of the sum of the 3 steps of the sequential extraction (AEC concentration + Organic concentration + Reducible concentration). These values are conservative; they

do not include trace metals or major elements residing in sulphides or silicates. An average value was plotted for the sites where duplicate samples were run.

Table 7. Pb, Zn, Ni, Cr and Cu Concentrations in the St. Clair Delta, Lake St. Clair, and Detroit River Sediments.

	Pb			Zn			Ni		
Analyte	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g
WI5	124	BD	BD	11	BD	33	4	2	BD
WI4	16	BD	BD	<1	BD	4	4	<1	17
LS21	20	BD	13	<1	78	17	6	BD	27
LS20	42	BD	4	43	<1	26	14	BD	56
LS19	16	BD	5	BD	35	34	9	BD	12
LS16	16	BD	9	BD	46	36	4	BD	17
LC17	117	21	52	328	<1	299	40	7	54
LS18	18	BD	4	10	42	37	5	BD	16
LS10	14	BD	11	2	71	8	5	BD	21
LS09	26	BD	7	3	48	37	8	BD	23
LS8	17	BD	16	BD	24	13	7	<1	190
LS24	20	4	4	BD	BD	60	6	<1	26
DT28	46	BD	23	33	BD	3	12	BD	6
DT29	30	BD	4	9	36	BD	16	4	17
DT32	4	BD	3	BD	BD	103	<1	BD	59
DT34	12	BD	3	19	17	BD	4	BD	14
DT33	22	3	5	26	BD	BD	6	BD	14

	Cu			Cr		
Analyte	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g
WI5	BD	6	BD	BD	19	21
WI4	6	5	BD	<1	BD	14
LS21	5	7	14	<1	BD	24
LS20	BD	18	20	3	60	49
LS19	BD	<1	7	2	BD	10
LS16	BD	3	10	<1	BD	14
LC17	8	17	91	28	25	116
LS18	4	2	5	<1	BD	12
LS10	BD	5	12	<1	BD	20
LS09	BD	6	16	BD	BD	18
LS8	2	4	7	<1	4	16
LS24	4	3	7	<1	3	21
DT28	6	7	BD	4	BD	<1
DT29	4	10	14	2	6	29
DT32	2	3	9	BD	4	121
DT34	BD	5	BD	<1	<1	11
DT33	4	5	9	<1	<1	12

BD values are below detection.

The x-axis follows the downstream flow of water from the St. Clair delta to the mouth of the Detroit River. The bottom bar graph depicts the proportion of the element extracted from the three steps of the sequential procedure. The proportions were normalised to 100 % to more easily define trends and note shifts in these trends throughout the waterway. In the following discussion, previous studies are cited to compare concentrations of trace metals but it is important to note the diversity of sediment collection and extraction procedures used from study to study.

Trace Metal Concentration

High lead concentrations were found in the sediment at site WI-5 (124 μg/g) and LS17 (214 μg/g) in the St. Clair area (Figure 6). WI-5 is delta sediment and LS17 was collected from the lake centre. Aside from these two sites, Lake St. Clair sediment Pb concentrations ranged from 21 to 46 μg/g. These values are in good agreement with previous studies allowing for the differences in sampling and analysis. Kemp et al., (1975) cited 26.7 μg/g as the lake sediment average. Rossman (1988) reported a mean lead concentration of 68 μg/g in Lake St. Clair mud extracted with an HCl matrix. Mudroch et al., (1988) compiled a range of 7 to 67 μg/g from various studies (sampling and extraction procedures were not described). The lead concentrations in this and other studies is elevated with respect to background values published by Kemp et al., (1976). Kemp et al., (1976) had background values of 35 μg/g in soils, 27 μg/g in bluffs and 28 μg/g in baseline sediment, all of which were total concentrations. In Kemp's et al., (1976) study, sediment was collected from the Lake Erie basin, bluffs were sampled from the eroding shoreline of Lake Erie and soils were obtained throughout Essex county.

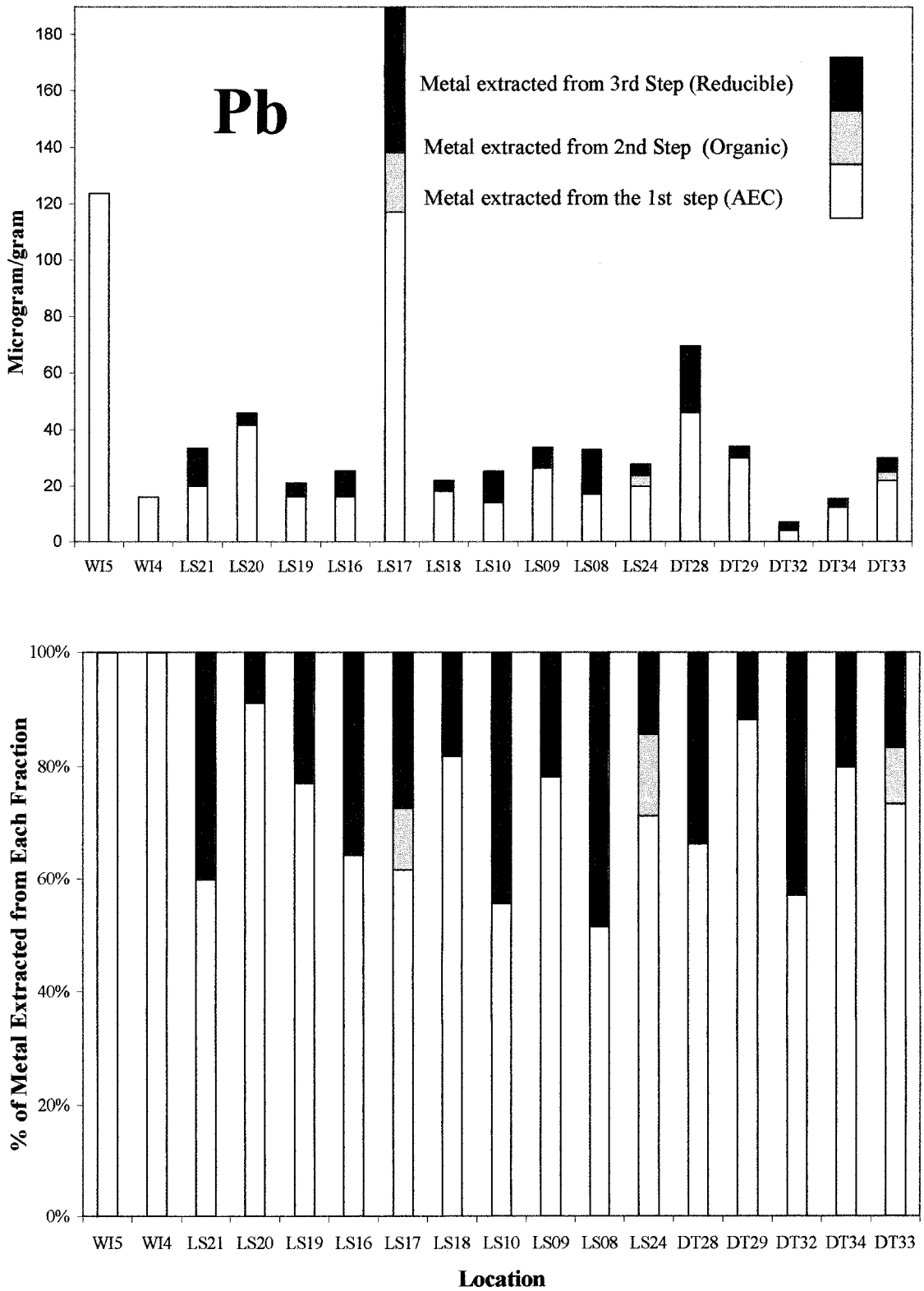

Figure 6. Concentration and Distribution of Pb in the St. Clair – Detroit River Waterway.

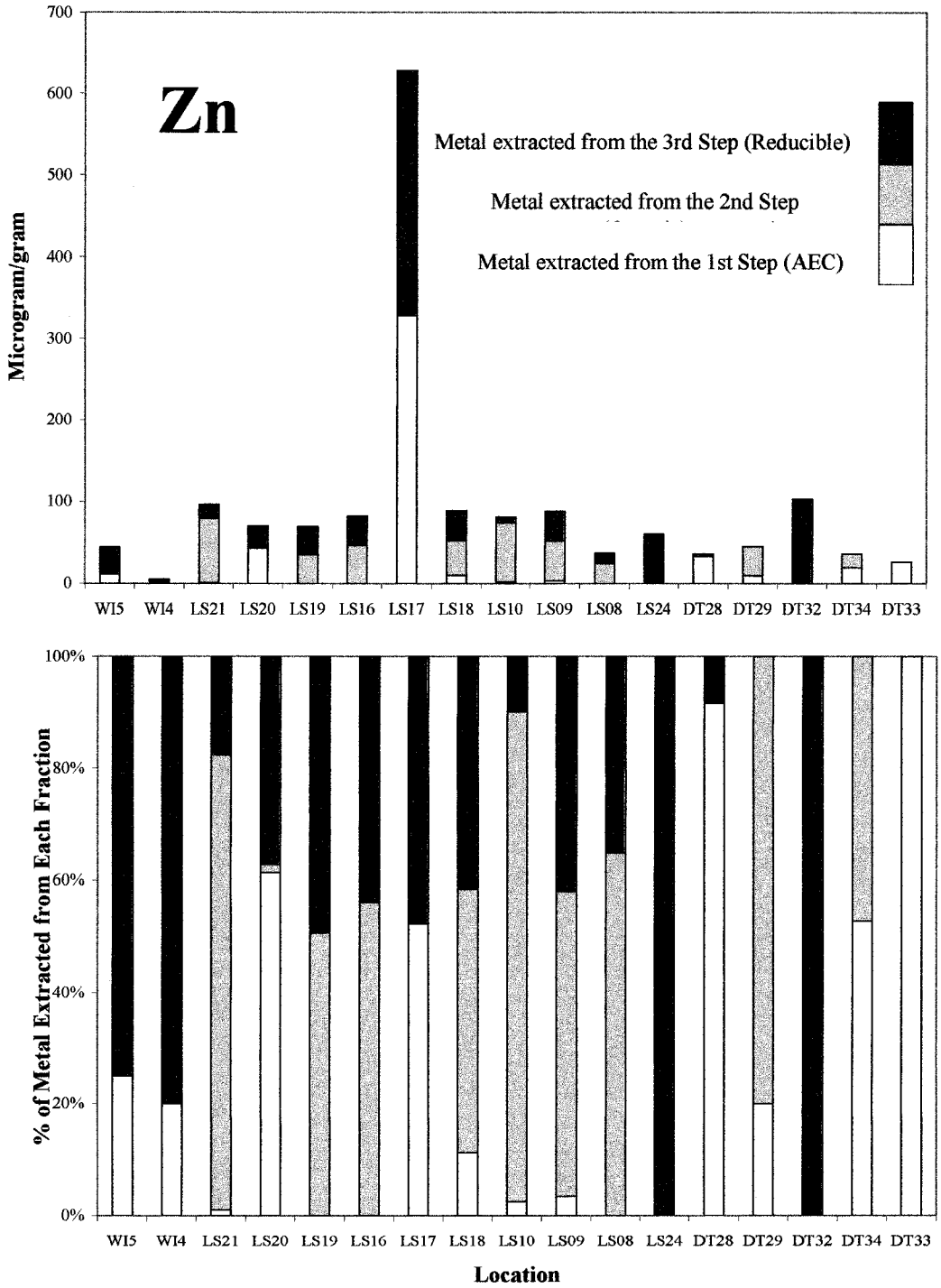

Figure 7. Concentration and Distribution of Zn in the St. Clair – Detroit Waterway.

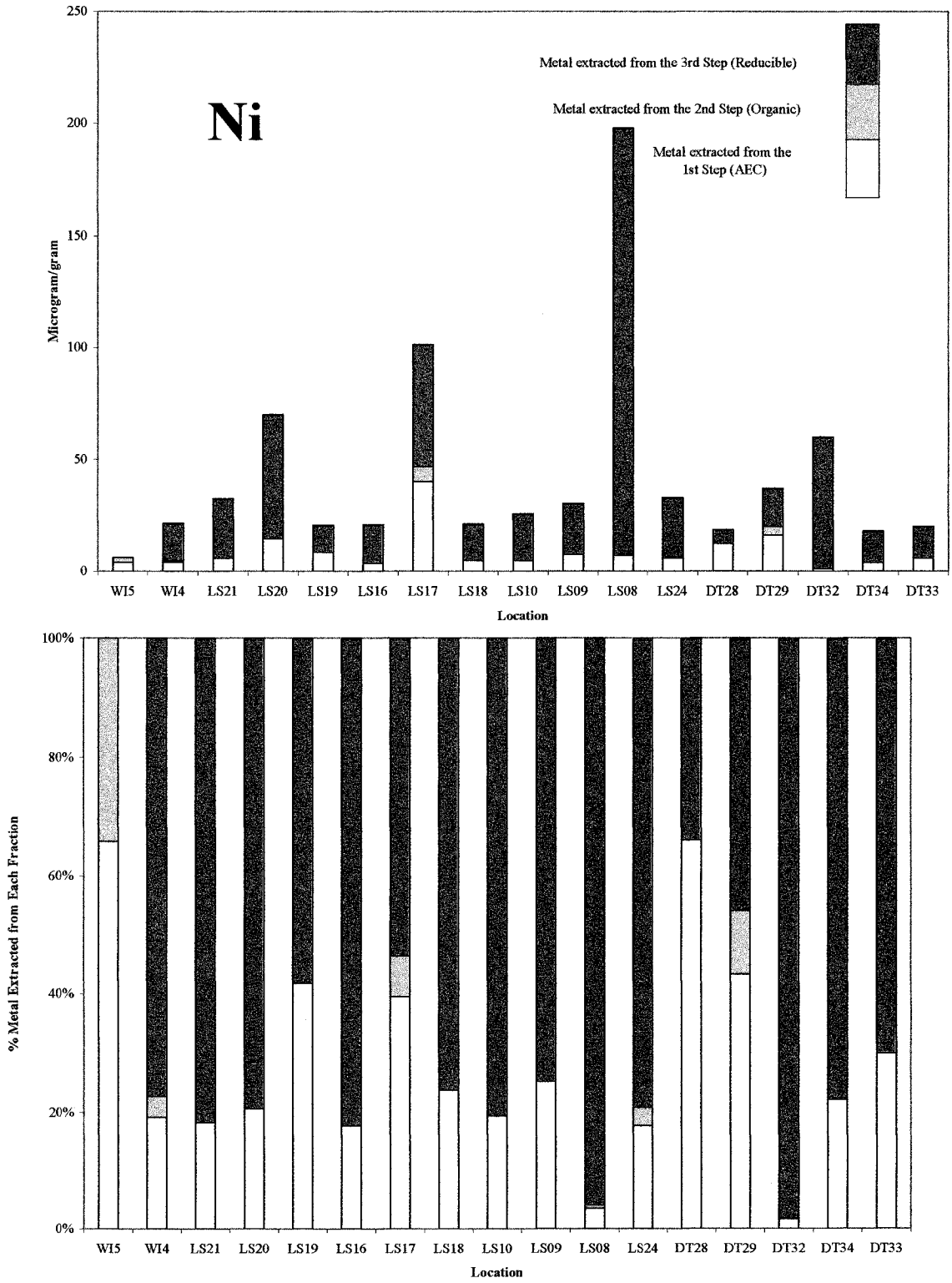

Figure 8. Concentration and Distribution of Ni in the St. Clair – Detroit River Waterway.

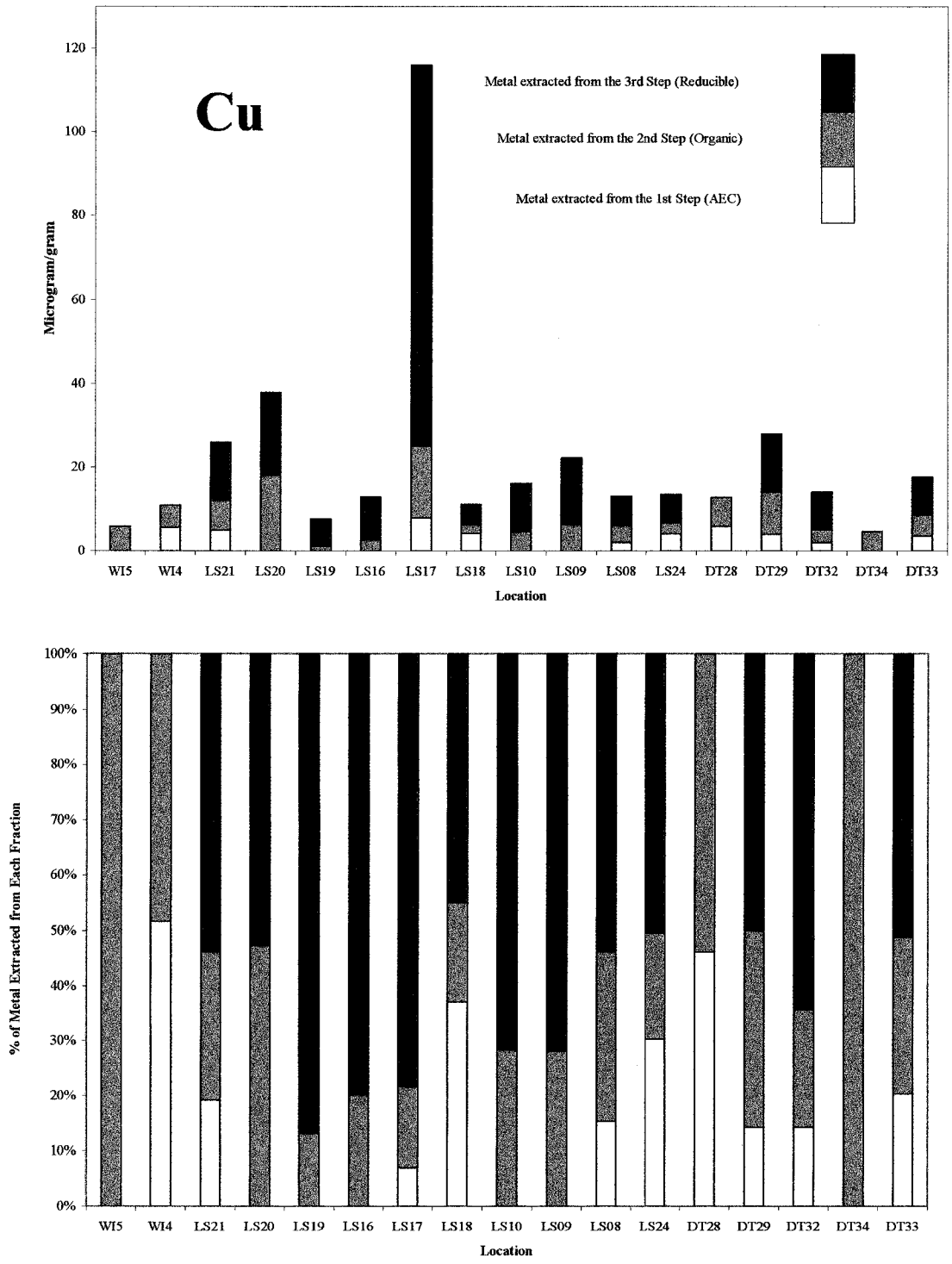

Figure 9. Concentration and Distribution of Cu in the St. Clair – Detroit River Waterway.

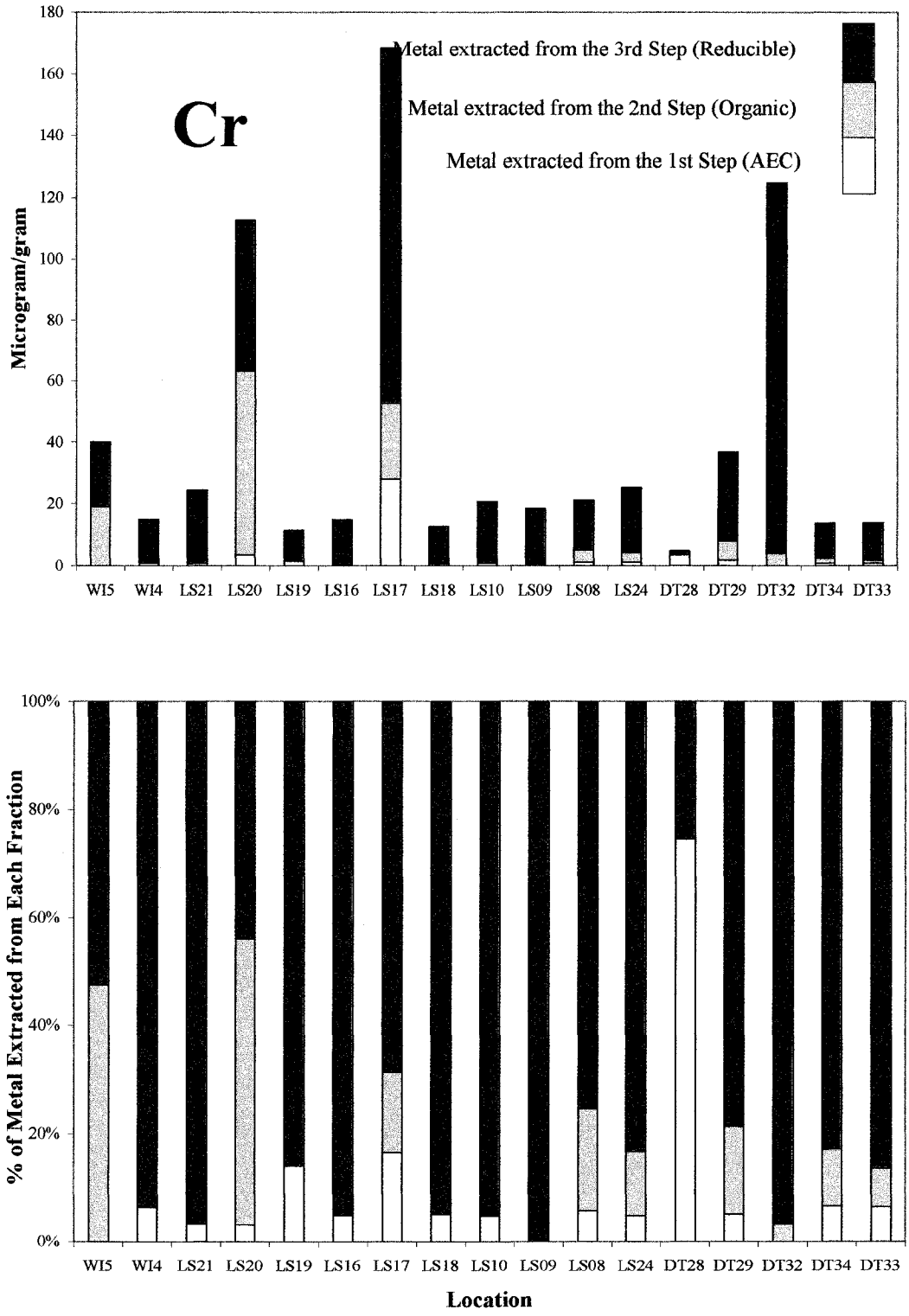

Figure 10. Concentration and Distribution of Cr in the St. Clair – Detroit Waterway.

Pb concentrations in Detroit River sediment ranged from 7 to 66 μg/g. DT28, located near the Windsor waterfront and across from Belle Isle, had the highest concentration at 66 μg/g. These values are low compared to previously published Pb concentrations. Fallon and Horvath (1985) reported slightly higher concentrations in bulk sediment samples, ranging from 3 to 73 mg/kg with lead hotspots in the Trenton channel and adjacent to Boblo Island (digestion procedure was not described). Hamdy and Post (1985) reported an average Pb concentration of 86 mg/kg with a maximum value of 760 mg/kg . Their concentrations were obtained on bulk samples with a partial HCl/HNO_3 acid digestion. Lead concentrations exceeded 200 mg/kg in the Trenton Channel, downstream of the Ecorse and Rouge Rivers, east of Fighting Island and along the Detroit and Windsor waterfronts. Mudroch (1985) reported a Pb average of 123 μg/g with a range of 14 to 704 μg/g (total sample digestion). In Mudroch's study, the Windsor waterfront had the highest lead concentration. Lum and Gammon cited a range of 2 to 96 μg/g in Detroit River sediment obtained on bulk samples with a partial 1N HCL acid digestion. Downstream of the Ecorse and Rouge Rivers were the most contaminated in their study with respect to Pb.

The highest concentration of zinc (Figure 7) was from site LC17 (627 μg/g) in Lake St. Clair sediment. Zn concentrations ranged from 7 to 627 μg/g with an average concentration of 122 μg/g in Lake St. Clair sediment. Previous studies on Lake St. Clair sediment reported lower zinc concentrations. Rossman (1988) cited 45 μg/g as a lake mud average; Thomas et al., (1975) reported 46.2 μg/g and in Mudroch et al., (1985) compiled a range of 8 to 107 μg/g from various sources.

Zn concentrations are lower in the Detroit River than in Lake St. Clair sediment; zinc concentrations ranged from 31 to 103 (site DT32) μg/g with an average value of 49 μg/g. Lum and Gammon (1985) found their highest concentrations of zinc, up to 104 μg/g, immediately downstream of the Ecorse River sediment. Mudroch (1985) reported zinc concentrations up to 338 μg/g along the Windsor waterfront and downstream of the Trenton Channel. Hamdy and Post (1985) calculated an average zinc value of 229 mg/kg in Detroit River sediment with the highest concentration at 2400 mg/kg. Kemp et al., (1976) published zinc concentrations of 75 μg/g in soils, 54 μg/g in bluffs and 98 μg/g in baseline Lake Erie sediment.

As with lead and zinc, the highest nickel concentration was from Lake St. Clair sediment (Figure 8), but unlike Pb and Zn, the highest concentration was extracted at LS08 (197 μg/g), near the Detroit River. LS17 had a Ni concentration of 101 μg/g. The average Ni concentration for Lake St. Clair sediment was 43 μg/g. Rossman, (1988) reported an average Ni concentration 17.6 μg/g and Thomas et al., (1979) reported an average concentration of 20.8 μg/g. Mudroch et al., (1988) compiled a range of 5 to 43 μg/g from previous research.

Downstream in the Detroit River sediment, nickel concentrations were lower with an average of 26 μg/g. None of the sample sites had any anomalous concentrations of nickel. Hamdy and Post (1985) reported an average Ni concentration of 28 μg/g and Mudroch (1985) reported 50 μg/g with a range of 21 to 83 μg/g. Lum and Gammon's (1985) highest Ni concentration was 37 μg/g collected at the mouth of the Ecorse River.

The average Cu concentration of Lake St. Clair sediment in this study was 28 μg/g (Figure 9). LS17 has the highest Cu concentration at 116 μg/g. Rossman (1988) reported 9.5 μg/g in baseline sediment and Thomas et al., 1976 cited 14.6 μg/g. A range of 2 to 48 μg/g was published by Mudroch et al., (1988). Kemp et al., (1976) published values of 27 μg/g for soils, 26 μg/g for bluffs, and baseline Lake Erie sediment has a Cu concentration of 29 μg/g.

Detroit River sediment had lower copper concentrations. The average Cu concentration was 26 μg/g. Mudroch (1985) reported an average value of 36 μg/g ranging up to 214 μg/g in the Trenton Channel and south of the Ecorse River. Hamdy and Post (1985) reported an average concentration of 51 μg/g with a peak at 380 μg/g. Lum and Gammon (1985) reported 44 μg/g as their highest concentration sampled at the mouth of the Ecorse River.

Cr concentration in sediment collected from the delta at WI-5, 40μg/g, is marginally higher relative to the Lake St. Clair sediment average of 39 μg/g (Figure 10). LS20 had a concentration of 112 μg/g, but with Zn, Pb, and Cu, Cr was the most concentrated at the lake centre (169 μg/g). Rossman (1988) reported an average baseline Cr concentration of 19.1 μg/g and Mudroch et al., (1988) published a range of values, 1 to 275 μg/g based on earlier research.

The Detroit River averaged 37 μg/g, with notable concentration of 125 μg/g at DT32. Hamdy and Post (1985) reported an average concentration of 43 μg/g Cr in Detroit River sediment, but their data had a wide range in concentrations (4 – 330 μg/g).

The highest concentration of Cr reported by Lum and Gammon (1985) in Detroit River sediment was 54 μg/g, found in sediment adjacent to the Ecorse River.

In summary, the highest concentrations of Pb, Zn, Ni, Cu, and Cr in sediment in this study were found in Lake St. Clair sediment. Pb, Zn, Cu, and Cr had the highest concentrations at LS17 and Ni was most highly concentrated in sediment proximal to the Detroit River (LS08). Site DT32, south of Fighting Island, contained the highest concentrations of Zn, Ni and Cr in Detroit River sediment, and conversely, the lowest values of Pb and Cu. Pb and Cu were more concentrated further upstream in sediment from DT29 and DT28.

Trace Metal Distribution

During the first step of the sequential extraction, 51 to 100% of the Pb was released from sediment (Figure 6). Notably, St. Clair Delta sediment released Pb entirely in the first step. LC17, LS24 and DT33 released a minor proportion of lead from the organic step. The remainder of lead, between 0 and 49 %, was associated with the reducible fraction. Figure 7 shows a complex pattern of Zn distribution among the three steps of the extraction. The other metals (except Cu) were primarily removed by one of the sequential steps. In Lake St. Clair sediment, Zn appears to partition between the organic and reducible fraction at all sites except for LS20 and LC17. Zinc was extracted from the first and last steps of the sequential procedure at sites LS20 and LS17.

53 to 96% of nickel released in the sequential extraction was liberated in the final step of the reaction (Figure 8). A minor to moderate amount of Ni is associated with the AEC fraction, (up to 40 %), but there is no spatial trend to this distribution. Ni extracted

from the organic fraction is virtually absent from the sediment except for WI-5, WI-4 and DT29

Copper was most abundantly released during the last step of the extraction. There is a pattern to Cu partitioning throughout the waterway (Figure 9). Copper in Lake St. Clair sediment is overwhelmingly released during the last step of the reaction with moderate contributions from the organic step of the sequential procedure whereas in Detroit River sediment, Cu partitioning shifts to more labile forms of the metal.

Between 52 to 100% of Cr was liberated in the last step of the extraction (Figure 10). Chromium was extracted from the organic step in minor to moderate amounts (< 20% of the total proportion of chromium released), sporadically in St. Clair delta and lake sediment, but increasingly from Detroit River sediment. A small percentage of Cr was released in the first step of the extraction in all but three samples (Figure 13).

Major Element Concentration

Table 8 lists Mg, Ca, Fe and Mn concentrations in sediment between the three sequential extraction steps. These elements are displayed in bar graphs as previously described for the trace metals (Figures 11 - 14).

The pattern of Mn, Mg, and Ca concentrations are almost identical (Figure 11, 12 and 13). LS20 has the highest concentrations of acid-extractable Ca, Mg and Mn. Iron is the anomaly; iron concentrations are high at LS20 and LS17 in Lake St. Clair sediment (Figure 14).

Major Element Distribution

Magnesium was released from the sediment in all three steps of the extraction, but most of it was recovered during the third step of the extraction (Figure 11). The

remaining magnesium is associated with the AEC fraction of the sediment. Trace amounts were released from the organic step of the extraction.

Table 8. Mg, Ca, Mn and Fe Concentrations in the St. Clair Delta, Lake St. Clair and Detroit River Sediments.

	Mg				Ca			
Analyte	Pore-Water µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g	Pore-water µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g
WI5	8	4428	961	10827	44	13463	1214	12144
WI4	13	9000	926	24516	74	25734	1446	36538
LS21	9	11521	871	22703	36	45749	1231	33884
LS20	6	35621	3939	105270	24	68693	6281	159307
LS19	8	8527	392	9419	37	26986	520	15047
LS16	BD	11351	1139	33259	BD	47949	1476	54869
LC17	23	5223	930	17824	70	37477	1304	26909
LS18	6	9767	637	16859	26	27234	767	27011
LS10	10	8631	841	15774	45	39072	880	23186
LS09	BD	12159	1188	34839	BD	42082	1445	56449
LS08	5	13464	1174	28709	19	54085	1614	45209
LS24	9	6416	905	15850	47	30960	1071	19862
DT28	22	10086	986	3091	91	27218	1406	5341
DT29	39	9645	1100	16036	178	36976	1399	19293
DT32	8	7838	1051	13129	41	36094	1310	18027
DT34	8	8423	1120	19521	36	42426	1228	29759
DT33	15	10595	939	19499	110	38056	1019	28051

	Mn				**Fe**			
Analyte	Pore-water µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g	Pore-water µg/g	AEC Fraction µg/g	Organic Fraction µg/g	Reducible Fraction µg/g
WI5	<1	122	9	172	<1	2640	3181	18403
WI4	<1	150	7	177	<1	947	1541	14628
LS21	<1	324	9	286	<1	680	1452	23397
LS20	BD	878	32	884	0	3105	4810	58950
LS19	<1	227	3	111	BD	1287	590	9643
LS16	BD	328	11	237	BD	1190	1308	15734
LC17	1	425	21	413	1	4779	3922	54349
LS18	1	223	6	181	1	1275	1140	13157
LS10	<1	368	13	232	<1	1164	2330	19042
LS09	BD	422	16	285	BD	2138	2406	18257
LS08	1	403	14	258	1	1721	2050	17122
LS24	1	401	15	238	1	1198	2655	20832
DT28	2	457	11	30	1	2527	2082	787
DT29	1	508	16	297	1	1752	3275	26925
DT32	<1	219	10	204	<1	1000	1331	19236
DT34	<1	321	16	184	<1	1134	2892	13250
DT33	<1	420	13	293	<1	1458	2916	24196

BD values are below detection

The first step of the extraction removed the majority of the calcium from the sediment (Figure 12). This was anticipated since this step was designed to dissolve carbonates. A moderate amount was released with the last step of the sequential procedure. A minor fraction of the calcium was associated with the organic fraction (< 5%) in all the samples.

As anticipated, most of the iron in the sediment, (75 to 90%) was removed by the final reaction of the procedure (Figure 14). The remaining portion of iron was released in roughly equal amounts during the first and second steps of the reaction. Slightly more than half of the manganese released from the sediment was recovered from the AEC step of the reaction (Figure 13). The remainder of Mn was recovered in the third step with less than 5% released from the organic step.

Ca, Mg, Fe and Mn were selected for study based on their occurrence in the sediment. Ca and Mg are primary constituents of carbonate minerals, namely dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$), common in sediment in the lower Great Lakes region. These two elements should be preferentially released during the first step of the sequential extraction designed to remove carbonates. Though the majority of Ca is recovered from the first step, and more than 50 % of the Mg is recovered during the last step of the reaction. Fe and Mn, the predominant elements forming hydrous oxyhydroxides in an aqueous environment, should be recovered most effectively during the last and most chemically reducing step of the extraction. As anticipated, most of the iron is released from the sediment in the last step but more than 50% of the manganese is liberated from the sediment during the first step of the extraction. The bulk of the remaining Mn is recovered with iron in the last step.

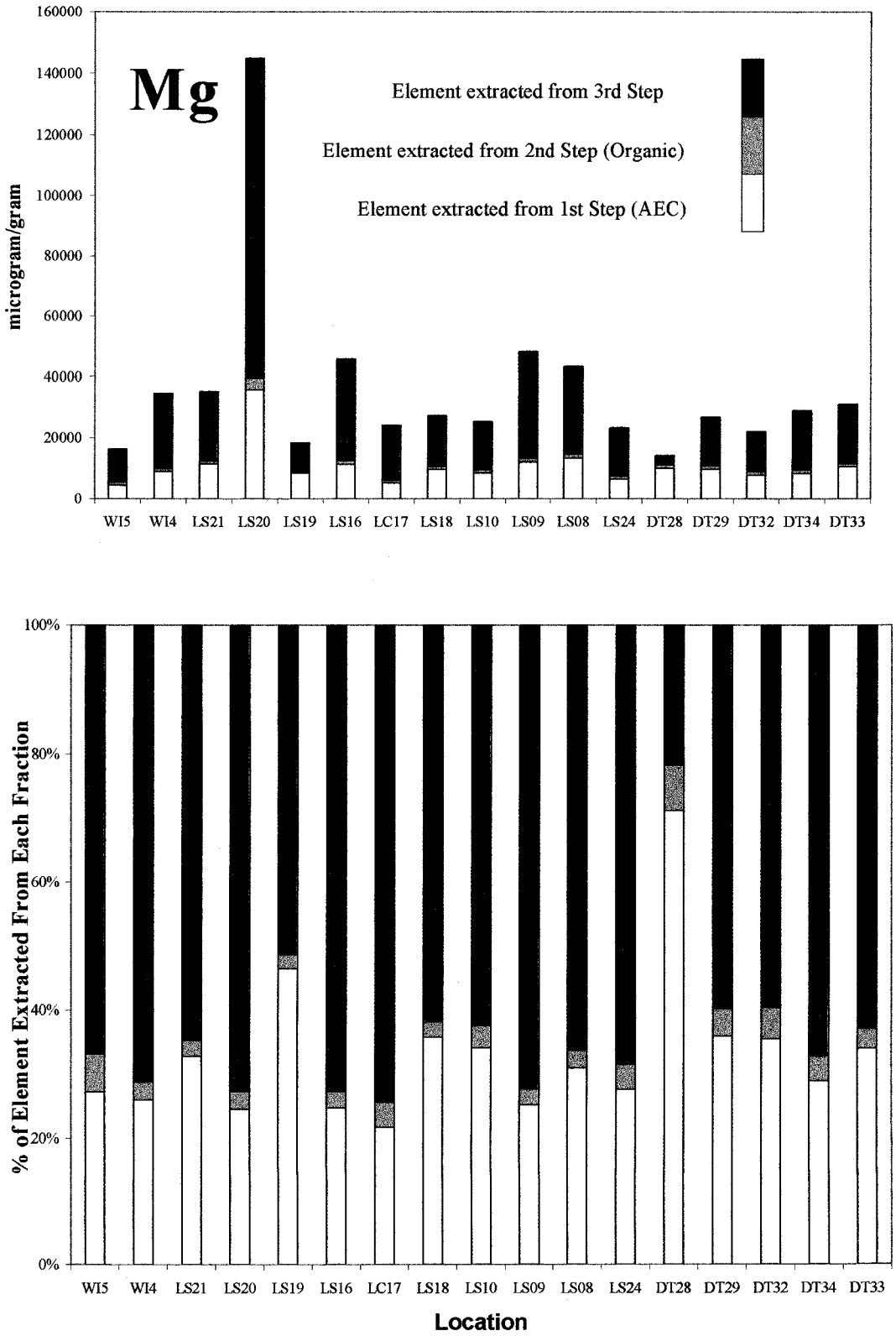

Figure 11. Concentration and Distribution of Mg in the St. Clair – Detroit River.

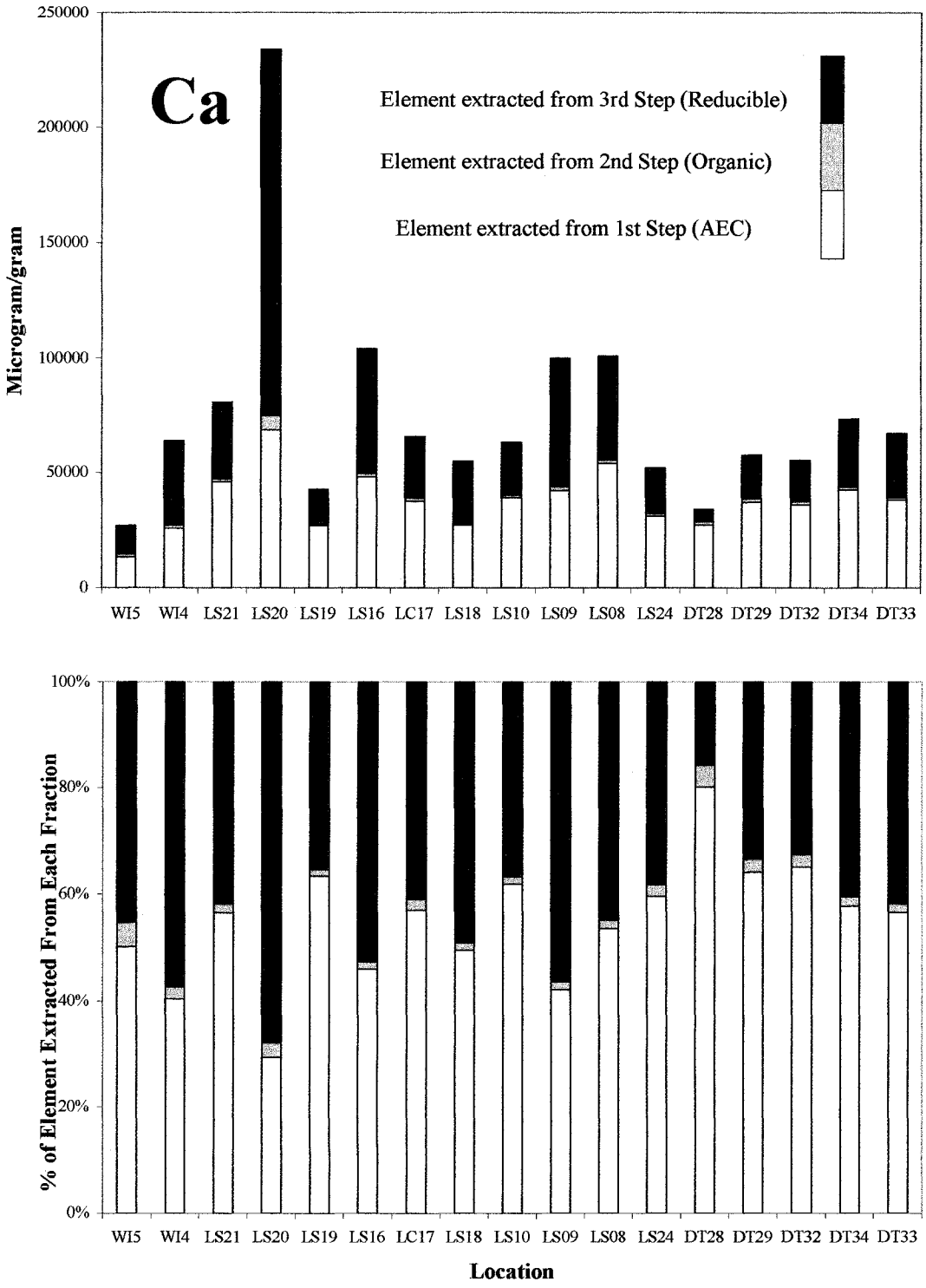

Figure 12. Concentration and Distribution of Ca in the St. Clair – Detroit River Waterway.

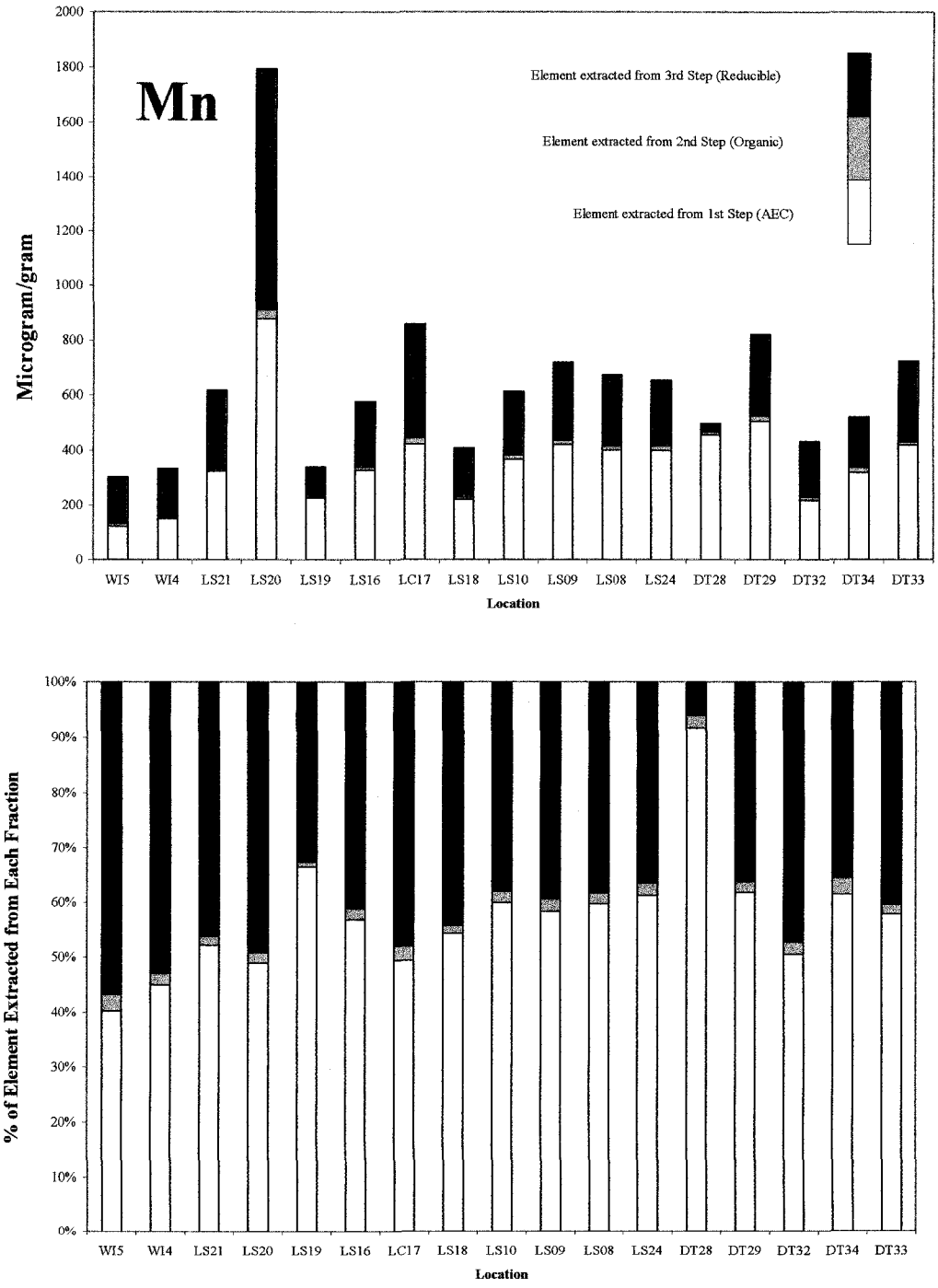

Figure 13. Concentration and Distribution of Mn in the St. Clair – Detroit Waterway.

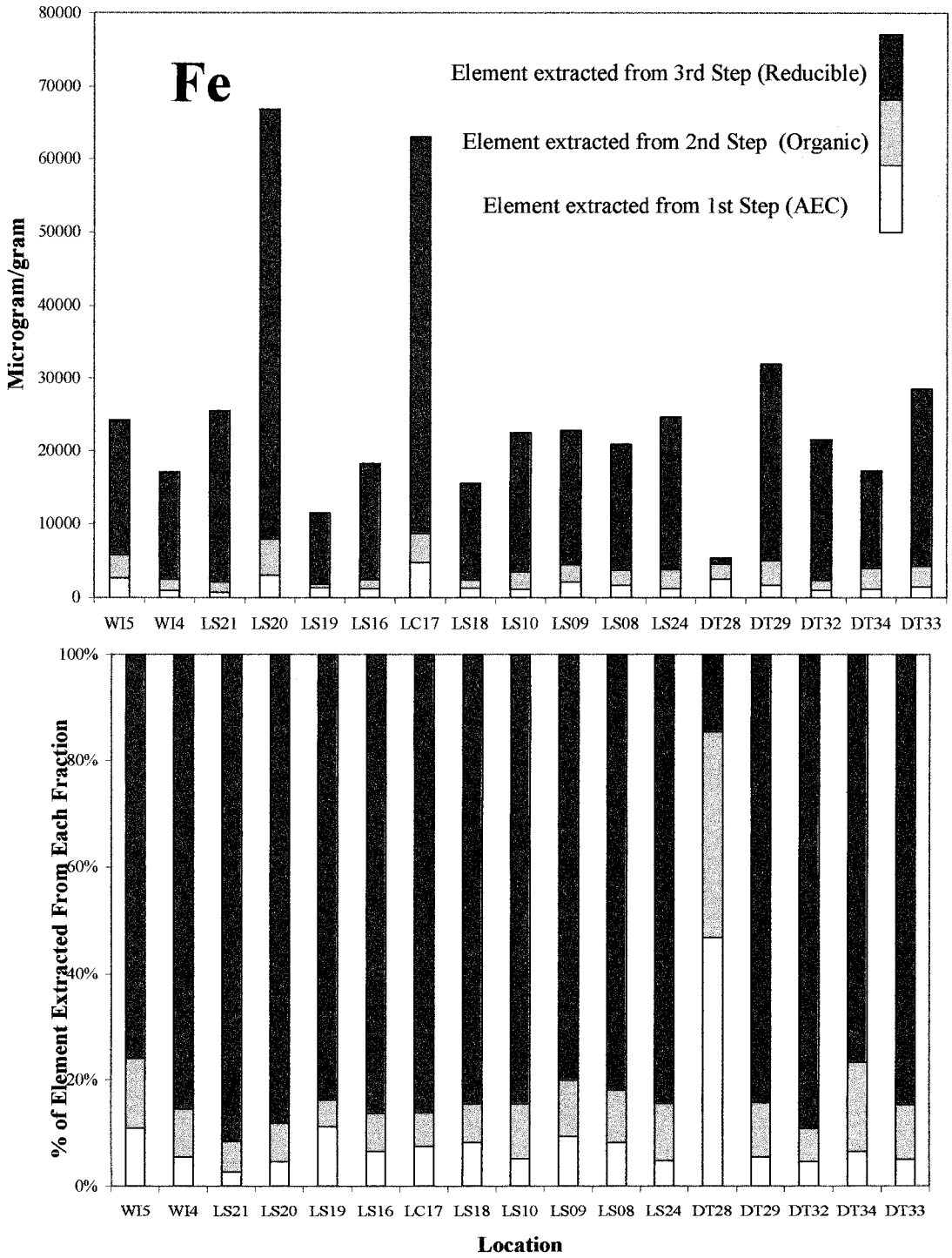

Figure 14. Concentration and distribution of Fe in the St. Clair – Detroit River Waterway.

TOTAL ELEMENT ANALYSIS

Precision and Accuracy

Precision and accuracy calculations for SY-4 (n=2) and LKSD-4 (n=5) are detailed in Appendix 10. Precision values in relative standard deviation for SY-4 and LKSD-4 and absolute deviation from certified (SY-4) and provisional (LKSD) values are listed below in Table 9.

Table 9. Accuracy and Precision of SY-4 and LKSD-4 for the Total Fusion Determinations.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
SY-4										
Accuracy %	3.6	3.2	2.3	1.9	3.1	14.8	2.1	0.7	1.9	136
% RSD	1.7	0.1	0.07	2.7	1.1	0.5	0.4	2.0	<1	<1
LKSD4										
Accuracy %	4.1	9.2	3.5	1.6	0.8	8.92	0.5	24	40	165
% RSD	1.9	1.7	1.2	1.8	1.8	2.5	1.2	1.8	<1	5.2

Na_2O and P_2O_5 had poor accuracy values but precision was excellent. Low concentrations may have contributed to the poor readings, but a bias must have been introduced in the procedure or analysis.

The total element determinations for 13 samples run are expressed as percent oxides in the following Table 10. Table 11 also includes phosphorous and LOI values.

Table 10. Total Major Element Concentration

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LOI
WI5	55.38	10.71	3.76	3.03	4.59	0.77	2.52	0.65	0.04	0.25	14.00
WI4	55.45	8.81	3.64	6.45	9.41	0.87	2.34	0.61	0.05	0.29	12.00
LS20	51.86	7.57	3.29	6.14	8.22	0.81	1.91	0.64	0.06	0.30	12.00
LS19	51.85	9.73	3.81	4.43	7.17	0.83	2.39	0.58	0.06	0.35	18.00
LS16	45.43	8.06	3.52	6.22	11.37	0.84	2.09	0.63	0.07	0.35	18.00
LC17	50.81	7.80	3.36	6.23	8.81	0.84	1.97	0.57	0.06	0.27	19.00
LS18	48.05	12.03	5.06	4.24	7.10	0.67	2.82	0.64	0.07	0.47	18.00
LS10	48.68	10.23	4.33	4.66	8.83	0.76	2.48	0.62	0.09	0.47	19.00
LS8	61.18	10.61	6.66	5.24	10.30	0.81	3.74	0.81	0.11	0.59	5.00
LS24	44.71	8.08	15.63	3.66	7.59	0.59	1.94	0.49	0.12	0.74	16.00
DT28	48.36	11.75	5.17	4.41	7.89	0.65	2.74	0.66	0.09	0.47	18.00
DT32	46.51	8.40	3.99	5.44	9.87	0.95	2.09	0.59	0.07	0.31	21.00
DT33	48.12	10.31	4.47	4.75	7.60	0.74	2.50	0.62	0.08	0.41	20.00

TOTAL CARBON, NITROGEN AND SULPHUR ANALYSES

Concentrations of total carbon (TC), nitrogen and sulphur are shown in Table 12. Nitrogen concentrations from the study area were less than 0.20% and sulphur concentrations were negligible.

The TC concentration from sediment collected from Walpole Island was 5.23%. This value is slightly higher than the concentrations of carbon sampled from Lake St. Clair and the Detroit River sediment. Carbon values in Lake St. Clair ranged from 3.89% (Site LS19) to 4.41% (LS24) with an average of 4.17% and a standard deviation of 0.20. Carbon values in the Detroit River sediment range from 4.25% to 4.63% with an average of 4.44% and a standard deviation of 0.16. Carbon concentrations from Lake St. Clair and the Detroit River are higher than values measured in the Western Basin of Lake Erie, 2.93% (Thomas et al, 1976 and Macfarlane, 1998).

Table 11. Concentration of nitrogen, carbon, and sulphur in sediment collected from Walpole Island, Lake St. Clair and the Detroit River.

Sample	Nitrogen %	Carbon %	Sulphur %
WI-4	0.23	5.23	0.00
LS19	0.15	3.89	0.04
LS18	0.21	3.95	0.00
LS16	0.08	4.20	0.00
LS17	0.11	4.38	0.00
LS09	0.15	4.09	0.00
LS08	0.26	4.25	0.00
LS24	0.28	4.41	0.00
DT29	0.27	4.63	0.00
DT30	0.20	4.25	0.00
DT32	0.11	4.44	0.03
DT33	0.24	4.43	0.00

MINERALOGY

X-RAY DIFFRACTION

Five samples, producing a series of 31 slides, were examined qualitatively by XRD. Two samples were studied from the Detroit River sediment (DT28 and DT32) and two from Lake St. Clair sediment (LS09 and LS18) and one from the St. Clair Delta (WI-5). At all the sites, XRD scans identified quartz, dolomite, clay minerals with sporadic occurrences of calcite, chlorite and illite. Calcite was identified in XRD scans in sediment collected from LS18 and DT32. Dolomite was removed from the sediment during the first step of the reaction (the step designed to remove carbonates) only from WI-5 and LS18; it was not until the final and strongest step of the extraction in LS09, DT32, and DT28 that dolomite peaks in the XRD scans disappear. Calcite was effectively removed from the sediment during the AEC extraction. The raw diffraction data is listed in Appendix 11.

CHAPTER 6

DISCUSSION

The goals of this study were to evaluate a sequential extraction with sediment of the Lake St. Clair – Detroit River waterway and the examine affinities between metal concentrations and distributions among the different sediment fractions. Metal concentrations and distributions were scrutinised in context with other characteristics of the sediment substrate including grain-size, total carbon, and total major element data. For the sake of clarity, tables 13 to 21 referred to throughout this chapter, are located at the end of this chapter.

EVALUATION OF THE SEQUENTIAL EXTRACTION

Sequential extraction procedures have been criticised for reagent non-selectivity and element redistribution (Xiao-Quan and Bin, 1993). Previous sequential extraction studies have used dried and milled sediment (mostly estuarine and deep sea mud), 'model' soils, and other geologic media (Tessier et al., 1979, Tipping et al., 1985, Xiao-Quan, et al., 1993, Hall et al., 1996*a*, 1996*b*). Test studies with spiked 'model' sediments demonstrated elemental redistribution to the extent the original site of metal adsorption and precipitation could not be determined with any reasonable certainly (Guy et al., 1978, and Kheboian and Bauer, 1987). It should be pointed out, that these model sediments are mixtures of doped (spiked with a particular element in the laboratory) and undoped phases. The metal-doped sediment is not in equilibrium with the undoped phases and the model sediment may be biased toward trace metal re-distribution (Xiao-Quan and Bin, 1993). Tipping et al., (1985) did not use 'model' sediment' but mine wall deposits in a sequential extraction and discovered that the release of lead was not related

at all to the original distribution in the sample media (Tipping et al., 1985, Xiao-Quan, et al., 1993). Aside from the inherent analytical problems, results may also be influenced by the duration of the experiment, temperature, ratio of solid matter to volume of extraction solution, choice of reagent, the extraction sequence, sample handling and pre-treatment (de Groot, et al, 1982, Rapin et al., 1986).

The sequential procedure adopted in this study was selected so that data obtained from LSKD-4 could be compared to previously published LKSD-4 concentrations from similar extractions. Preliminary results of trace metal reproducibility (Pb, Ni, Cu, Zn, and Cr) with SEDA are excellent; total (sum of the values obtained from the three fractions) precision RSD values are between 5 to 10%. Since SEDA is more representative of sediments examined in this study, the precision reflects favourably on the reliability of the study data. The preliminary results of major element reproducibility (Ca, Mg, Fe and Mn) were acceptable for SEDA; all values were less than 15% RSD.

LSKD-4's precision results were also excellent for Pb, Zn, Ni totals. LKSD-4's Zn reproducibility, however, suggests a problem in the methodology or possibly re-adsorption/ remobilization of zinc. It is not an outlier that is skewing the data; the RSD reflects the consistently wide range of Zn values obtained. The RSD values for Zn in the three extraction steps were 33% (AEC), 67% (Organic), and 29% (Reducible) compared to SEDA's zinc precision of 5% (AEC), 13% (Organic) and 9% (Reducible). Sample heterogeneity and procedural contamination may have contributed to this anomaly, but it is unlikely since heterogeneity and contamination should have affected the other trace metal RSD values. There was zinc contamination in one blank for Batch 2; the AEC Blank reported 310 μg/g. Results from Batch 2 however, were not included in LKSD-

4's precision calculations; this contamination cannot account for the spread of zinc concentrations reported in the sediment and LKSD.

Reagent selectivity proved to be problematic with carbonate removal. The AEC step dissolved calcite as witnessed by the disappearance of calcite peaks from the XRD diffractograms. The pH of the Na-acetate (Table 12) was well within the range needed to ensure the complete dissolution of calcite (Han and Banin, 1985).

Dolomite dissolution however, was sporadic. By the end of the first 6 hour Na-acetate leach, dolomite was dissolved from WI-5 and LS08. The second exposure to sodium acetate removed dolomite from DT28. LS09 and DT32 however, still had dolomite in the sediment prior to the final step. WI-5 and LS08 had high proportions of siliceous material, (54% and 44%, respectively) and DT28 had 44% sand. LS09 and DT32, however, considerably lower percentages of sand-sized particles, 13% and 14 %, respectively. It appears that the Na-acetate solution dissolved dolomite in the samples with a higher proportion of siliceous material. The Na-acetate leach may have become supersatured with respect to calcium and was unable to continue dissolving in the finer grained fractions as possibly indicated by the lower pH reading below in Table 12.

Table 12. Initial and Final pH of the Na-Acetate Reagent.

	AEC		Organic		Reducible	
Batch	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
1	5.2	5.2	10.4	8.7	1.0	0.9
2	5.2	5.2	10.3	9.4	1.1	1.0
5	5.2	5.2	10.2	9.7	1.1	1.2
6	5.2	5.3	10.2	9.6	N/A	N/A
8	5.2	5.3	10.1	9.7	1.0	1.3
10	5.2	5.2	10.1	10.1	1.1	1.1
11	5.2	5.3	10.1	10.0	1.1	1.0
Avg		5.2		9.6		1.1

The final pH measurements were recorded at the end of the second reaction with each reagent

This does not necessarily imply a grain-size correlation since the quantity of dolomite in the study samples is unknown. Kemp, et al., (1976), reported the Lake Erie and Lake Ontario shoreline buffs contained an average of 2.4 % dolomite. Lake Erie sediment contained an average of 5.0% dolomite. Up to 4% detrital and authigenic carbonates (calcite and dolomite) were reported in sediment from St. Clair Delta samples (Blackburn, et al., 1997).

It is possible that the crystal chemistry of dolomite is affecting its solubility. The drop from higher energy deltaic conditions to a lower energy lacustrine setting may selectively winnow detrital dolomites of differing density possibly due to different element substitution in the lattice. For example, heavier ferroan dolomites, deposited preferentially in the channels of the St. Clair Delta and in the swift waters proximal to the Detroit River channel, may have solubilities differing from non-ferroan dolomites.

The sample weight to volume ratio in this study was 1:20 (0.5g wet sediment:10 mL of 1.0 M NaOAc). Sediment was reacted with the reagent for 6 hours at room temperature, rinsed with MilliQ water and then subjected to another six hours with fresh NaOAc. The dolomite disappeared from the samples collected from sandier substrates while it remained in the finer-grained samples. In Tessier et al. (1989), the sample weight to volume ratio was 1:8 (1g dry and milled river sediment to 8 mL NaOAc) and the sediment was exposed to the reagent at room temperature for 5 hours before the dolomite was completely dissolved. It should be noted that Tessier's sediment came from rivers whose sediment source was Precambrian rock whereas sediment in this study was chiefly eroded Palaeozoic strata (Tessier et al. (1989)). Han et al., (1985) concluded that a NaOAc–HOAc buffer solution at pH 5.5 with a solid to solution ratio of 1:25 could

not removed all the dolomite after 16 hours, (Han et al., (1985) used carbonate-rich (up to 50%) caliche soils).

A stronger reagent, in combination with hotter temperatures and/or longer reaction times, is needed to dissolve dolomite from sediment. Unfortunately, dissolving dolomite may extract not only adsorbed, exchangeable and carbonate-associated metals, but also metals bonded to other fractions in the sediment. If trace metals are not associated with dolomite in the sediment, the dissolution of this mineral in the last step of the extraction may be acceptable provided the dissolution of dolomite does affect that step of the extraction.

Table 13 lists regressional values of elements released during the AEC step of sequential extraction. Since this step is designed to dissolve carbonates, a positive correlation should exist between Ca and Mg. Ca, Mg and Mn in Lake St. Clair sediment are positively correlated. Aside from the carbonate dissolution, Mn oxides may also be susceptible to dissolution as they preferentially precipitate in the higher pH microzones adjacent to carbonates (Lee, 1975). These relationships are weak to non-existent in Detroit River sediment, suggesting that Lake St. Clair sediment may contain more carbonates.

Table 14 lists the regressional values of elements released during the second step of the sequential procedure designed to complex with organic material. This step releases elements by removing the stabilising cations within organic complex. The positive correlation between Mg, Ca, Fe and Mn and % C in Lake St. Clair sediment suggestions this step is effective. Once again, correlations are weak to absent in Detroit River sediment.

Table 15 lists regressional values between elements extracted in the last step of the sequential extraction designed to destroy Fe-Mn oxides. In Lake St. Clair and Detroit River sediment, positive relationships exist between Fe and Mn and Mn, Mg, and Ca due to the destruction of Fe-Mn oxides and possibly the final dissolution of dolomite. The positive correlation between and Al, Ca, and Mn may be the product of clay mineral disintegration. In the Detroit River, Al is positively correlated with Mn and Fe. This relationship may be due to clay mineral disintegration or the presence of Al hydroxides associated with the Fe-Mn oxides in the Detroit River sediment.

DISTRIBUTION OF TRACE METALS

Though partitioning is operationally defined, the procedure still provides insight into the geochemical behaviour of trace metals in the St. Clair – Detroit River waterway. The different metal distribution environments of Lake St. Clair and the Detroit River are evident from the sequential extraction data.

Prior to a discussion of trace metal partitioning, some useful observations can be made with the major element, grain-size, and carbon data with respect to the Lake St. Clair and Detroit River sediment. In Table 16, positive relationships exist between certain elements extracted from the sequential procedure (AEC step) and the major oxides obtained from total fusion. In Detroit River sediment, Fe and Mn are positively correlated with Al_2O_3, Fe_2O_3, K_2O, TiO_2, MnO and P_2O_5 and negatively correlated with MgO, CaO, Na_2O and LOI. Al_2O_3, Fe_2O_3, K_2O, TiO_2, and MnO concentrations reflect clay mineralogy and the extractable Fe and Mn suggests that Fe-Mn colloids/oxides are inextricably associated with clay minerals. Al_2O_3, Fe_2O_3, K_2O, TiO_2, and MnO are negatively correlated with the < 63 μm grain-size fraction. CaO, MgO and Na_2O are

positively correlated with the < 63 μm grain-size fraction. This suggests that the carbonate content of the sediment increases with a decrease in particle size. Drawing a few conclusions, Fe-Mn oxides, and their link to clay minerals and phosphorous loading from sewage treatment plants, may be the most important sink for easily adsorbed metals in the Detroit River. No such trends could be established in Lake St. Clair sediment.

LEAD

In a study of river sediment in Quebec, Tessier et al., (1980), discovered that most of the lead was associated Fe-Mn oxyhydroxides; moderate amounts were found with carbonates and as residual material. Virtually no lead was liberated by an exchangeable step (Tessier's study employed $MgCl_2$ to release exchangeable metals). McKee et al., (1989) found lead was preferentially associated with Fe/Mn oxides in lacustrine environments in the Great Lakes region. Coastal marine sediment studies have also indicated that lead is preferentially associated with Fe-Mn oxides and may occur in high concentrations (up to 870 ppm) in Fe/Mn nodules (Gupta, et al., 1975, Morgan et al., 1964). The majority of lead in this study, was released as an exchangeable, adsorbed or carbonate-associated metal.

A correlational analysis of Pb with major element oxides obtained from total fusion (Table 19) and other metals and elements released from the sequential extraction (Table 19) highlights two different environments where lead exists as a labile metal. In Lake St. Clair sediment, AEC extractable lead is weakly correlated with MgO, whereas in Detroit River sediment, Pb has a strong positive correlation with Al_2O_3, Fe_2O_3, K_2O, TiO_2, MnO, P_2O_5 and a strong negative correlation with MgO, Na_2O, CaO and LOI. Lead in Lake St. Clair sediment may be carbonate-bound. In Detroit River sediment,

lead appears to be adsorbed to clay, Fe/Mn oxides and phosphate-rich loadings into the river system.

Reducible Pb in Lake St. Clair sediment is also linked with MgO (Table 21). In Detroit River sediment, Pb has a strong positive correlation with Fe_2O_3, MnO but is negatively correlated with MgO, Na_2O and CaO (Table 21). The reducible step of the extraction procedure possibly released lead from the remaining carbonates that did not dissolve during the AEC step in Lake St. Clair sediment. Pb released from the destruction of Fe/Mn oxides in the Detroit River sediment suggests Fe-Mn oxides adsorb Pb and possibly incorporate Pb. The presence of iron in Detroit River sediment as Fe oxides plays a greater role in retaining adsorbed and possibly co-precipitated iron than Lake St. Clair sediment.

ZINC

Zn partitioned preferentially with the Fe-Mn sediment fraction in the delta and Detroit River sediment samples. This was anticipated as Morgan, (1964) and Jenne (1968), found Fe-Mn oxides are excellent scavengers of zinc. Tessier, et al., (1980) reported zinc predominantly associated with Fe-Mn oxides with minor contributions from the exchangeable, carbonate and organic sediment fractions. Organically-bound zinc however, is a moderate to important factor in Lake St. Clair sediment.

Based on the relationships between Zn and the major element oxides totals in Table 19, clays and Fe-Mn oxides exert the same influence on the AEC fraction of Zn as with Pb. In Lake St. Clair sediment, the organic step of the sequential extraction mobilised a considerable proportion of the total acid extractable zinc, but in Table 14, zinc concentrations indicated a negative relationship with the total carbon content in Lake

St. Clair sediment and a strongly positive relationship with total carbon in Detroit River sediment. Zinc may possibly be entering Lake St. Clair waterway in complexed or chelated form, whereas zinc is complexing with the organic material in the Detroit River sediment. As with lead, co-precipitation with Fe-Mn oxides, locks zinc into reducible sediment fraction.

NICKEL

In Tessier et al., (1980) most of the extractable Ni was found in the Fe-Mn oxide fractions with low contributions from the exchangeable, carbonate and organic fractions. Ni and Fe-Mn oxide associations are acknowledged in the literature (Jenne, 1968, Morgan et al., 1964) as Ni is commonly found in high concentrations in ferro-manganese nodules. Most of the Ni extracted in this study was also liberated from the reducible phase.

In the AEC step, Ni is positively correlated with SiO_2, K_2O and TiO_2 in Detroit River sediment and negatively correlated with these oxides in Lake St. Clair sediment (Table 19). Most of the Ni was released during the reducible step of the sequential extraction, but that may be a result of the complete dissolution of carbonates or degradation of clay minerals. Correlations between Ni and Fe_2O_3 and MnO are negative to non-existent (Table 21) and between Ni and Fe/Mn are non-existent (Table 15).

COPPER

Because of the propensity of copper to form stable complexes with organic matter, a high portion of Cu was anticipated from the organic step of the extraction. Tessier et al., (1980), found a high percentage of soluble copper was found bound to organic matter with appreciable amounts in the Fe-Mn oxide and carbonate fractions. In

this study however, most of the copper was associated with Fe-Mn oxides, followed by organically-bound and AEC extractable copper.

In the AEC step of the extraction, Cu was released as an adsorbed metal from Fe/Mn oxides and clay minerals (Table 19) from Detroit River sediment. As anticipated, correlations were weak with Lake St. Clair sediment. From the organic step of the extraction, Cu exhibits weak relationships with major element chemistry in Lake St. Clair sediment, but has strong positive relationships with SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, MnO and P_2O_5 and strong inverse relationships with MgO, Na_2O, CaO and LOI (Table 21) in Detroit River sediment. In Table 14, Cu (along with Zn and Ni) is positively correlated with carbon in Detroit River sediment. Clay minerals and Fe-Mn oxides may be intermixed or flocculated with organic matter giving rise to these relationships.

Cu extracted from the reducible step in Detroit River sediment is positively linked to LOI (incomplete destruction of OM from the second step?), MgO and Na_2O, and negatively correlated with the oxides indicative of clay minerals and Fe/Mn oxides (Table 21). Copper does not appear to co-precipitated or incorporated with Fe-Mn oxides, unlike the previous metals.

CHROMIUM

The majority of Cr in the sediment from the St. Clair – Detroit waterway is associated with the reducible fraction of the sediment. With the minor concentrations extracted from the AEC step, Cr has an affinity in Detroit River sediment for SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, MnO and P_2O_5 as with previous trace metals suggesting Cr is held as an adsorbed metal on clays, Fe/Mn oxides and phosphorous inputs into the waterway (Table 19).

In the Organic step of the extraction, chromium behaved opposite to Cu in Detroit River sediment; Cr is related to MgO, CaO, Na_2O and LOI (Table 20) suggesting it complexes with organic matter and may possibly be associated with carbonates. Cr in Lake St. Clair sediment is strongly correlated to Mg, Ca, and to a lesser extent Mn, and Fe (Table 14). In the reducible extraction, Cr in Detroit River sediment had the same relationships as copper.

TRACE METAL BEHAVIOUR IN THE SEDIMENT FRACTIONS

The absolute concentrations of trace metals extracted from the AEC step decrease in the order Pb>>Zn > Ni > Cu > Cr in the two Walpole Island samples and the Detroit River samples. In Lake St. Clair, zinc and nickel switch places; the decreasing order of absolute AEC concentration is Zn > Pb > Ni > Cu > Cr. Zn and Pb are predisposed to mobility in relation to the other metals examined. The preponderance of lead over suite of trace metals examined in sediment examined from Walpole Island strongly suggests anthropogenic loading near or upstream of the sample site.

The absolute concentrations of metals bound to the organic fraction of the sediment for Walpole Island decrease in the order of Cr > Zn > Cu > Ni > Pb. In Lake St. Clair the decreasing order is Zn > Cr > Cu > Pb > Ni. For Detroit River sediment, the pattern changes to Zn > Cu > Cr > Ni and Pb.

The absolute concentrations of metals associated with Fe-Mn oxyhydroxides in the sediment for the Walpole Island samples decrease in the sequence of Zn > Cr > Ni (Pb and Cu concentrations were below detection limits). In Lake St. Clair, the decreasing order is Ni > Cr > Cu > Pb > Zn and in the Detroit River sediment, the decreasing order is: Cr > Zn > Pb > Cu > Ni.

Table 13. Correlation co-efficients between Elements Extracted During the AEC Step of the SEQ Procedure.

Lake St. Clair Sediment AEC Extraction											
	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	% C	< 63 µm
Pb	1	**0.988**	**0.991**	0.687	**0.980**	-0.088	0.015	0.281	**0.931**	0.472	0.486
Zn		1.000	**0.983**	0.728	**0.997**	-0.208	-0.086	0.161	0.885	0.454	0.470
Ni			1.000	0.662	**0.981**	-0.086	-0.003	0.276	0.931	0.425	0.475
Cu				1.000	0.724	-0.386	-0.255	-0.197	0.447	0.541	-0.084
Cr					1.000	-0.237	-0.101	0.132	0.868	0.469	0.438
Mg						1.000	0.818	0.894	0.171	-0.346	0.105
Ca							1.000	0.850	0.213	0.388	-0.059
Mn								1.000	0.520	**0.820**	0.296
Fe									1.000	0.442	0.655

Detroit River Sediment AEC Extraction											
	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	% C	< 63 µm
Pb	1.000	0.708	0.829	0.860	**0.972**	0.751	-0.742	0.843	**0.986**	0.707	-0.649
Zn		1.000	0.299	0.465	0.685	0.733	-0.406	0.522	0.677	-0.218	-0.672
Ni			1.000	0.702	0.776	0.610	-0.439	**0.931**	0.768	**0.929**	-0.153
Cu				1.000	0.773	0.730	-0.865	0.694	0.883	0.626	-0.712
Cr					1.000	0.590	-0.760	0.738	**0.979**	0.857	-0.666
Mg						1.000	-0.378	0.833	0.672	0.132	-0.444
Ca							1.000	-0.338	-0.838	-0.102	0.884
Mn								1.000	0.749	0.705	-0.192
Fe									1.000	0.770	-0.739

Table 14. Relationships between Elements Extracted During the Organic Step of the SEQ Procedure.

Lake St. Clair Sediment Organic Extraction	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	Al	% C	< 63 μm
Pb	1.000	-0.521	**0.990**	0.590	0.274	-0.109	-0.090	0.302	0.466	-0.079	0.577	0.408
Zn		1.000	-0.554	-0.636	-0.732	-0.516	-0.542	-0.609	-0.640	0.240	-0.765	-0.472
Ni			1.000	0.570	0.260	-0.113	-0.094	0.302	0.463	-0.055	0.588	0.384
Cu				0.112	0.147	0.174	0.177	0.239	0.222	0.186	0.522	0.373
Cr					1.000	**0.900**	**0.917**	0.896	0.879	-0.095	0.579	0.386
Mg						1.000	**0.997**	0.875	0.771	0.112	0.590	0.240
Ca							1.000	0.862	0.763	0.042	0.612	0.217
Mn								1.000	**0.973**	0.335	**0.855**	0.432
Fe									1.000	0.297	**0.813**	0.490
Al										1.000	0.496	0.178

Detroit River Sediment Organic Extraction	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	Al	% C	< 63 μm
Pb	1.000	-0.370	-0.250	-0.193	-0.340	-0.733	-0.889	-0.100	0.297	0.340	-0.538	-0.080
Zn		1.000	**0.888**	0.743	0.697	0.731	0.373	**0.842**	0.688	0.496	**0.999**	0.686
Ni			1.000	0.857	0.802	0.446	0.445	0.567	0.552	0.197	**0.999**	0.484
Cu				1.000	0.393	0.194	0.484	0.567	0.636	0.077	**0.948**	0.072
Cr					1.000	0.576	0.379	0.260	0.131	0.102	**0.833**	0.690
Mg						1.000	0.468	0.596	0.192	0.353	0.765	0.710
Ca							1.000	-0.004	-0.248	-0.559	0.714	-0.155
Mn								1.000	**0.893**	**0.804**	**0.863**	0.628
Fe									1.000	0.787	0.608	0.447
Al										1.000	0.308	0.734

Table 15. Relationships between Elements Extracted During the Reducible Step of the SEQ Procedure.

Lake St. Clair Sediment Reducible Extraction	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	Al	% C	< 63 µm
Pb	1.000	**0.928**	0.222	**0.939**	0.883	-0.257	-0.269	0.073	0.520	-0.229	0.521	0.257
Zn		1.000	-0.004	**0.975**	**0.923**	-0.172	-0.180	0.141	0.578	-0.247	0.498	0.456
Ni			1.000	0.027	0.079	0.140	0.140	0.143	0.113	0.056	0.332	-0.121
Cu				1.000	**0.975**	-0.043	-0.055	0.289	0.702	-0.059	0.471	0.439
Cr					1.000	0.147	0.131	0.477	0.836	0.136	0.538	0.442
Mg						1.000	**0.999**	**0.928**	0.647	**0.879**	0.183	0.216
Ca							1.000	**0.916**	0.629	**0.863**	0.084	0.224
Mn								1.000	**0.878**	**0.881**	0.737	0.290
Fe									1.000	0.636	0.642	0.386
Al										1.000	0.687	-0.031

Detroit River Sediment Reducible Extraction	Pb	Zn	Ni	Cu	Cr	Mg	Ca	Mn	Fe	Al	% C	< 63 µm
Pb	1.000	-0.271	-0.463	-0.544	-0.429	-0.898	-0.829	-0.844	-0.830	-0.770	-0.044	**-0.922**
Zn		1.000	**0.977**	0.220	**0.975**	-0.120	-0.144	-0.012	0.102	0.013	-0.461	0.060
Ni			1.000	0.365	**0.996**	0.071	0.022	0.190	0.298	0.206	-0.407	0.262
Cu				1.000	0.399	0.369	0.173	0.810	0.885	0.893	**0.999**	0.494
Cr					1.000	0.019	-0.044	0.177	0.296	0.206	-0.327	0.248
Mg						1.000	**0.977**	0.838	0.759	0.734	-0.095	0.837
Ca							1.000	0.711	0.612	0.584	-0.437	0.746
Mn								1.000	**0.987**	**0.986**	0.498	0.775
Fe									1.000	**0.993**	0.743	0.757
Al										1.000	0.644	0.707

Table 16. Relationships among Major Elements Extracted during the AEC Step and Total Fusion Major Oxide Data.

Lake St. Clair Sediment AEC Extraction	Mg	Ca	Mn	Fe	< 63 µm	Detroit River Sediment AEC Extraction	Mg	Ca	Mn	Fe	< 63 µm
SiO_2	0.252	0.415	0.177	0.220	-0.069	SiO_2	**0.957**	-0.455	**1.000**	**0.807**	-0.717
Al_2O_3	-0.287	-0.405	-0.581	-0.505	-0.684	Al_2O_3	**0.815**	-0.714	**0.956**	**0.953**	**-0.901**
Fe_2O_3	-0.285	-0.289	-0.093	-0.331	0.495	Fe_2O_3	0.693	**-0.833**	**0.884**	**0.993**	**-0.966**
MgO	0.439	0.691	0.501	0.646	0.274	MgO	-0.875	0.631	**-0.983**	**-0.913**	**0.847**
CaO	0.031	0.519	0.060	0.014	0.385	CaO	**-0.998**	0.233	**-0.966**	-0.646	0.533
Na_2O	0.246	0.452	0.178	0.418	-0.152	Na_2O	-0.891	0.605	**-0.989**	**-0.899**	**0.828**
K_2O	-0.121	0.033	-0.330	-0.324	-0.263	K_2O	**0.853**	-0.664	**0.974**	**0.930**	**-0.869**
TiO_2	0.305	0.524	0.086	-0.071	-0.167	TiO_2	0.711	**-0.819**	**0.896**	**0.989**	**-0.960**
MnO	-0.277	-0.067	-0.125	-0.441	0.531	MnO	0.766	-0.769	**0.929**	**0.974**	**-0.933**
P_2O_5	-0.313	-0.256	-0.238	-0.558	0.329	P_2O_5	**0.850**	-0.669	**0.973**	**0.932**	**-0.872**
LOI	-0.460	-0.626	-0.398	-0.003	-0.203	LOI	-0.631	**0.876**	**-0.843**	**-0.999**	**0.984**

Table 17. Relationships among Major Elements Extracted during the Organic Step and Total Fusion Major Oxide Data.

Lake St. Clair Sediment Organic Extraction	Mg	Ca	Mn	Fe	Al	Detroit River Sediment Organic Extraction	Mg	Ca	Mn	Fe	Al
SiO_2	0.158	0.181	0.110	0.092	0.030	SiO_2	-0.854	-0.162	0.841	0.782	0.202
Al_2O_3	-0.483	-0.479	-0.654	-0.624	-0.199	Al_2O_3	-0.645	0.160	0.626	0.543	-0.120
Fe_2O_3	-0.197	-0.220	-0.070	-0.011	0.219	Fe_2O_3	-0.491	0.342	0.470	0.377	-0.303
MgO	0.518	0.524	0.580	0.487	0.120	MgO	0.727	-0.048	-0.710	-0.634	0.007
CaO	0.074	0.046	0.137	0.001	0.541	CaO	**0.953**	0.389	**-0.945**	**-0.906**	-0.426
Na_2O	0.209	0.233	0.168	0.091	-0.038	Na_2O	0.750	-0.014	-0.733	-0.660	-0.026
K_2O	-0.281	-0.280	-0.392	-0.416	0.067	K_2O	-0.696	0.091	0.679	0.600	-0.051
TiO_2	0.170	0.170	0.012	-0.099	0.162	TiO_2	-0.513	0.318	0.491	0.400	-0.279
MnO	-0.231	-0.270	-0.102	-0.083	0.580	MnO	-0.581	0.239	0.561	0.474	-0.200
P_2O_5	-0.304	-0.335	-0.250	-0.218	0.343	P_2O_5	-0.692	0.098	0.674	0.595	-0.057
LOI	-0.401	-0.401	-0.296	-0.203	-0.210	LOI	0.417	-0.418	-0.395	-0.299	0.381

Table 18. Relationships among Major Elements Extracted during the Reducible Step and Total Fusion Major Oxide Data.

Lake St. Clair Sediment Reducible Extraction						Detroit River Sediment Reducible Extraction					
	Mg	Ca	Mn	Fe	Al		Mg	Ca	Mn	Fe	Al
SiO_2	0.161	0.171	0.142	0.091	0.037	SiO_2	-0.245	-0.186	-0.302	-0.427	-0.312
Al_2O_3	-0.446	-0.433	-0.558	-0.644	-0.446	Al_2O_3	-0.541	-0.488	-0.589	-0.692	-0.598
Fe_2O_3	-0.258	-0.293	-0.235	-0.240	-0.017	Fe_2O_3	-0.688	-0.643	-0.730	-0.815	-0.737
MgO	**0.544**	0.570	0.587	0.636	0.291	MgO	0.442	0.387	0.494	0.606	0.504
CaO	0.108	0.138	0.016	-0.019	-0.054	CaO	0.011	-0.050	0.070	0.202	0.080
Na_2O	0.254	0.287	0.241	0.286	-0.002	Na_2O	0.412	0.356	0.465	0.579	0.475
K_2O	-0.253	-0.235	-0.377	-0.484	-0.332	K_2O	-0.481	-0.427	-0.532	-0.640	-0.541
TiO_2	0.216	0.245	0.066	-0.121	0.023	TiO_2	-0.670	-0.624	-0.713	-0.800	-0.720
MnO	-0.287	-0.310	-0.313	-0.377	-0.041	MnO	-0.607	-0.557	-0.652	-0.748	-0.660
P_2O_5	-0.348	-0.373	-0.401	-0.489	-0.111	P_2O_5	-0.487	-0.433	-0.538	-0.645	-0.546
LOI	-0.400	-0.402	-0.292	-0.074	-0.312	LOI	0.746	0.704	0.784	0.860	0.790

Table 19. Relationships among Trace Metals Extracted during the AEC Step and Major Element Oxides for Lake St. Clair and Detroit River Sediments.

Lake St.Clair Sediment AEC Extraction						Detroit River AEC Extraction					
	Pb	Zn	Ni	Cu	Cr		Pb	Zn	Ni	Cu	Cr
SiO_2	0.060	0.049	0.139	-0.063	0.062	SiO_2	0.883	**0.997**	0.893	0.873	0.776
Al_2O_3	-0.477	-0.403	-0.453	-0.072	-0.411	Al_2O_3	**0.986**	**0.971**	**0.990**	**0.983**	**0.936**
Fe_2O_3	-0.254	-0.265	-0.280	0.244	-0.245	Fe_2O_3	**1.000**	**0.910**	**0.999**	**1.000**	**0.985**
MgO	**0.542**	**0.504**	**0.522**	-0.007	0.486	MgO	**-0.962**	**-0.992**	**-0.967**	**-0.956**	-0.890
CaO	-0.009	0.008	-0.047	-0.212	0.016	CaO	-0.748	**-0.949**	-0.762	-0.734	-0.606
Na_2O	0.330	0.329	0.378	-0.257	0.338	Na_2O	**-0.952**	**-0.996**	**-0.958**	**-0.945**	**-0.875**
K_2O	-0.379	-0.331	-0.339	-0.095	-0.322	K_2O	**0.973**	**0.985**	**0.977**	**0.968**	**0.910**
TiO_2	-0.229	-0.224	-0.203	-0.274	-0.233	TiO_2	**1.000**	**0.920**	**1.000**	**1.000**	**0.981**
MnO	-0.407	-0.393	-0.422	0.044	-0.368	MnO	**0.996**	**0.949**	**0.998**	**0.994**	**0.961**
P_2O_5	**-0.503**	-0.488	**-0.520**	0.074	-0.469	P_2O_5	**0.974**	**0.984**	**0.979**	**0.969**	**0.912**
LOI	0.198	0.252	0.165	0.171	0.248	LOI	**-0.994**	**-0.872**	**-0.992**	**-0.996**	**-0.996**

Table 20. Relationships among Trace Metals Extracted during the Organic Step and Major Element Oxides for Lake St. Clair and Detroit River Sediments.

Lake St.Clair Sediment Organic Extraction						Detroit River Organic Extraction					
	Pb	Zn	Ni	Cu	Cr		Pb	Zn	Ni	Cu	Cr
SiO_2	-0.046	-0.129	0.099	0.167	0.170	SiO_2	0.393	-	-	**0.927**	**-0.992**
Al_2O_3	-0.424	**0.595**	-0.367	**-0.584**	**-0.561**	Al_2O_3	0.081	-	-	**0.998**	**-0.980**
Fe_2O_3	-0.045	-0.364	-0.079	-0.343	-0.273	Fe_2O_3	-0.107	-	-	**0.992**	**-0.926**
MgO	0.346	-0.188	0.387	0.681	0.575	MgO	-0.193	-	-	**-0.985**	**0.996**
CaO	-0.019	0.201	0.058	0.010	-0.091	CaO	-0.598	-	-	-0.812	**0.936**
Na_2O	0.165	0.106	0.232	0.373	0.282	Na_2O	-0.225	-	-	**-0.978**	**0.999**
K_2O	-0.353	0.321	-0.217	-0.416	-0.406	K_2O	0.149	-	-	**0.991**	**-0.992**
TiO_2	-0.348	0.236	-0.203	-0.037	0.007	TiO_2	-0.082	-	-	**0.995**	**-0.935**
MnO	-0.211	-0.044	-0.173	-0.431	-0.408	MnO	0.000	-	-	**1.000**	**-0.961**
P_2O_5	-0.295	-0.040	-0.282	-0.555	-0.475	P_2O_5	0.143	-	-	**0.992**	**-0.991**
LOI	0.289	0.314	0.162	-0.093	-0.241	LOI	0.189	-	-	**-0.978**	0.891

Table 21. Relationships among Trace Metals Extracted during the Reducible Step and Major Element Oxides for Lake St. Clair and Detroit River Sediments.

Lake St.Clair Sediment Reducible Extraction						Detroit River Sediment Reducible Extraction					
	Pb	Zn	Ni	Cu	Cr		Pb	Zn	Ni	Cu	Cr
SiO_2	0.202	-0.066	**0.882**	0.040	0.057	SiO_2	0.668	**-0.989**	**-1.000**	-0.600	**-0.999**
Al_2O_3	-0.286	-0.414	0.149	-0.452	**-0.530**	Al_2O_3	0.870	-0.892	-0.953	-0.823	**-0.935**
Fe_2O_3	-0.261	-0.119	0.045	-0.285	-0.241	Fe_2O_3	**0.947**	-0.792	-0.880	**-0.915**	-0.853
MgO	**0.503**	0.385	0.228	**0.546**	**0.568**	MgO	-0.809	**0.937**	**0.981**	0.754	**0.969**
CaO	0.229	-0.025	0.426	0.062	0.011	CaO	-0.475	**0.996**	**0.968**	0.395	**0.980**
Na_2O	0.407	0.212	0.249	**0.370**	0.322	Na_2O	-0.789	**0.949**	**0.987**	0.731	**0.977**
K_2O	-0.097	-0.372	**0.726**	-0.360	-0.412	K_2O	0.834	**-0.921**	**-0.972**	-0.782	**-0.958**
TiO_2	-0.028	-0.348	**0.796**	-0.224	-0.225	TiO_2	**0.938**	-0.807	-0.892	**-0.904**	-0.866
MnO	-0.219	-0.313	0.420	-0.391	-0.373	MnO	**0.907**	-0.853	**-0.926**	-0.866	**-0.904**
P_2O_5	-0.377	-0.378	0.252	**-0.509**	-0.491	P_2O_5	0.837	**-0.919**	**-0.970**	-0.786	**-0.956**
LOI	0.131	**0.329**	-0.913	0.256	0.165	LOI	**-0.970**	0.739	0.838	**0.945**	0.807

CHAPTER 7

CONCLUSIONS

The goals of this thesis were to evaluate a procedure that could be applied to the study of trace metal partitioning in sediment and determine partitioning and concentration of Pb, Zn, Ni, Cu and Cr within the sediments of the Lake St. Clair – Detroit River area.

The precision of LKSD-4, a certified reference material of homogenized lake sediment, and SEDA, the in-house reference material consisting of Great Lake sediment, was good to excellent when run through the sequential extraction procedure. The reproduceability of the results with the sequential extraction in comparison to other partial and total extractions showed the procedure as useful. The closest RDS values were obtained from the AEC extraction. The ORG and RED extractions had more variance but the values reported for some of the trace metals were so close to detection limits that RSD may not be the appropriate tool to quantify precision. SEDA precision was also excellent with RSD values under 10% except for Ni (15% RSD). Only zinc reproduceability was problematic. Zn readings in the blanks run in Batch 2 may have been contaminated in the AEC and RED steps and this contamination may be responsible for the skewed RSD values.

LKSD-4 and SEDA however, were air-dried and ground to a homogenous powder. The sediment in this study was collected wet, frozen and then used for study. The samples were mixed shortly after collection and prior to freezing but the samples may not have been as homogeneous as the reference materials. Translating precision to a wet sediment with a variable carbonate content also presents a challenge. Extraction procedures need to be tailored to the sediment that is under study. Continuous sampling

of the selected sites on a yearly basis would not only provide insight to metal mobility, but by retaining and utilising sample material from previous years, one could establish an in-house reference material with which chart future changes specific to the Detroit River – St. Clair waterway.

The highest metal concentrations were found in samples collected from Lake St. Clair. LS17, the site with the highest metal values, was collected within the deeper part of the lake and adjacent to shipping to channels. The sediment collected at this site had a reddish hue, consisted of silty laminations and was very fine-grained. Ninety-seven percent of the material from the sample was finer than 63 μm fraction (highest percentage of fine-grained material of all the samples collected next to DT29 at 98%). Pb, Zn, Cu and Cr values were highest at this location. Pb was released primarily in the AEC fraction, whereas the remaining three metals were extracted from the RED step of the procedure. The highest Ni concentrations in Lake St. Clair were recorded at LS09 and were also the highest values reported in the study area for nickel. The nickel was released primarily from the RED step in the extraction. LS09 is located near the Canadian shore in shallow waters. The sample contained abundant Zebra shells, coarser pebbly material, and was considerably more silty that the lake centre.

In comparison to previous studies such as Mudroch et al., (1988), Mudroch et al., (1985), Kemp et al., (1975), Rossman (1988), the total metal concentrations extracted from this study were higher than geological baseline for trace metals; Pb and Cr were lower or marginally within previous established ranges. Ni, Cu, and Zn recorded higher concentrations than in the previously listed studies.

Total metal concentrations decreased downstream in the study area. The Detroit River sediment had a high proportion of the more labile forms of trace metals than in Lake St. Clair. Correlations between trace metal concentration and major element oxide data and major element sequential data indicated that Fe-Mn oxides, clay minerals, and phosphorus provided the primary reaction sites for adsorbed metals in the Detroit River substrate. The highest Pb and Cr concentrations were recorded at DT28, a well-sorted black brown silty clay with 56% of the sediment in the < 63 μm fraction. The highest Cu, Zn and Ni concentrations were collected from the DT32 site. DT28 lies adjacent to the Windsor waterfront, south of Bell Isle. The DT32 sediment sample consisted of a black silty material with abundant weeds with 86% of the sample below 63 μm sediment fraction. DT32 sample site lies south of Fighting Island and adjacent to Turkey Island in the Detroit River, a previous disposal site for waste products from the manufacture of caustic soda and soda ash.

Citing previous studies on trace metal values in the Detroit River, Rossman (1988), Mudroch et al., (1988), Lum and Gammon (1985), Mudroch (1985), and Hamdy and Post (1985), Pb, Zn, Ni, and Cu concentrations sampled in this study were low. Only Cr (DT32 location) recorded a higher value than in previous studies of Detroit River sediment. Pb, as with the St. Clair sediment samples, was released primarily from AEC fraction with approximately 30% from the RED step. Zn is the anomaly in the study; the other trace metal were released primarily from one phase (PB – AEC and Ni, Cr, and Cu favoured the RED phase). Zinc was removed from all phases in different proportions from different sites. LS17 sample had 50% of its zinc mobilised from the AEC step with the remainder released during the RED step. The DT32 sample released zinc in the

final RED step. Perhaps the contamination discussed earlier in the procedural analysis has imprinted over the results. The remaining metal suite (Ni , Cr and Cu) generally favoured the RED step of the extraction. Copper showed a more pronounced variance, but most CU was released during the RED step.

Anthropogenic inputs of metals into a waterway would be expected to increase the total concentration of the metal in the system and alter the ratio of residual metal to the total of the metal extracted. The highest concentrations of Pb, Zn, Cu and Cr and the second highest concentrations of Ni were obtained from sample LC17 near the centre of Lake St. Clair. This may suggests a temporary repository for metal accumulation. More metal loading may also be occurring in the Detroit River, but the residence time may be considerably shorter than the Lake St. Clair. Of all the metals selected for study, lead would a primary concern since it appears the most mobile and in the highest concentrations especially in Lake St. Clair and Walpole Island. Whether the lead is a product of the petrochemical or other industrial sources or perhaps from localized lead shot, its concentration and mobility lends itself to continued study. Long term sampling is needed at the same sites utilising the same techniques in order to understand how long metals stay in the sediment or how metals transport.

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APPENDIX 1

Sequential Extraction Procedure

Reagents

The sodium acetate reagent used in the first AEC phase, ("AnaLar" grade from BDH), was made by dissolving 82.03 g per 1 L of de-ionised water. The solution was adjusted to pH 5.0 with concentrated HNO_3, "Analar Grade" at room temperature (22.5°C). The sodium pyrophosphate reagent (Sigma "ACS Reagent") used in the second phase of the procedure designed to liberate metals from the organic fraction, had a strength of 0.1 M (adjusted to pH 10.0 with concentrated HNO_3) and was made by dissolving 44.6 g per 1 L of de-ionised water. The reagent used in the last reducing step was made by dissolving 69.49 g of hydroxylamine hydrochloride ("Assured" quality from BDH) in de-ionised water. The pH of the solution was adjusted to 2.0 with concentrated nitric acid.

Adsorbed, Exchangeable and Carbonate Step (I)

0.5 g of dewatered sediment was placed into a 50 mL polypropylene centrifuge tube. 10 mL of 1.0M NaOAc (sodium acetate), adjusted to pH 5.0 with concentrated HNO_3, was added to the centrifuge tube and the tube was agitated for 6 hours at room temperature. After six hours, the solution was filtered into pre-weighed 60 mL polypropylene Nalgene containers. 2.5 mL of de-ionized water was added to the sediment, shaken, and then centrifuged at 6 000 rpm for 10 minutes. The water was decanted and added to the initial supernatant collected from the sample. Another 2.5 mL was added to the test-tube following the same rinsing procedure as outlined above. This water was also added to the initial supernatent. After the second rinse with de-ionized water, another 10 mL of Na-acetate was added to the sediment and the above described

extraction sequence was repeated. The two steps in this extraction were added together (along with the rinses) and analysed as one aliquot. After the last rinse, the total mass of the supernatant was recorded.

Organic Step (II)

Following the AEC procedure, 35 mL of 0.1M $N_4P_2O_7$ (sodium pyrophosphate) adjusted to pH 10.0 with concentrated HNO_3, was added to the test-tube. The test-tube was shaken at room temperature for 1 hour. Following the agitation, the solution was centrifuged at 6 000 rpm for 10 minutes. The supernatant was filtered from the sediment into new pre-weighed 125 ml polypropylene Nalgene containers. Another 35 mL of sodium pyrophosphate was added to the sediment and reacted for 1 hour at room temperature while agitated. After 1 hour, the test-tube was centrifuged at 6 000 rpm for 10 minutes and the clear supernatant was added to the corresponding sample container by filtration. The sediment was then twice rinsed with 2.5 mL of de-ionized water and centrifuged at 6 000 rpm for 10 minutes. The rinse water was added to the supernatant. The total volume of supernatant was recorded.

Reducible Step (III)

15 ml of 1.0M NH2OH.HCl (hydroxylamine hydrochloride), adjusted to pH 2 with HCl, was added to the previously rinsed sediment. The test-tubes were placed into a water-bath, heated to 90°C, for three hours. The caps of the test-tubes were finger-tight; every half hour the tubes were carefully loosened to release the gas build-up and then were agitated by hand. After 3 hours, the tubes were centrifuged at 6 000 rpm for 10 minutes and the supernatant was filtered into cleaned 60 mL

l polypropylene Nalgene containers. The sediment was rinsed with 5 ml of 25% HOAc (acetic acid) in de-ionized water, centrifuged at 6 000 rpm for 10 minutes, decanted and added to the initial supernatant from this step. The rinse procedure was repeated again with another 5 mL of the HOAc solution. Following the last decant, another 15 mL of the reagent was reacted with the sediment for 1.5 hours at 90°C. After 1.5 hours, the test-tube was centrifuged and rinsed twice with 5 mL of 25% HOAc as described above. The rinses were added to the recovered reagent.

APPENDIX 2

Operating Conditions of the ICP-OES

Pre-Integration Time	15 seconds
Off-Peak Integrations	2 seconds
On-Peak Integrations	3 seconds
Integration Time	4 seconds
Forward Power	1100
Sample Type	Aqueous
Intermediate Flow	1.2
Carrier Gas Flow	0.5
Tranport Pump Speed	2.0
Analysis Pump Speed	2.0
Transport Time	40.0
Nebulizer Pumped	No

Analytical Lines

Report Name	Units	Channel	PMVolt	BG1	BG2	Lambda Node (nm)	PMT	Shutter	APL
Na	ppb	250	700	-88	96	589.001	1	0	0
Mg	ppb	98	650	-96	96	279.077	2	2	0
AL	ppb	117	700	-88	96	308.216	4	0	0
K	ppb	210	850	-88	104	766.488	1	1	0
Ca	ppb	126	500	-144	144	317.934	3	1	0
Cr	ppb	93	1000	-72	80	267.716	4	1	0
Mn	ppb	84	700	-80	80	257.611	3	2	0
Fe	ppb	86	450	-80	80	259.939	4	2	0
Ni	ppb	58	950	-80	88	231.605	5	2	0
Cu	ppb	129	950	-72	88	324.754	2	1	0
Zn	ppb	32	700	-96	88	213.857	7	1	0
As	ppb	11	1000	-80	80	193.761	7	0	0
Hg	ppb	12	1000	-96	88	194.228	7	4	0
Pb	ppb	40	950	-96	88	220.355	0	1	0
V	ppb	107	1000	-88	80	292.402	5	0	0
Co	ppb	54	1000	-88	88	228.617	5	1	0
Cd	ppb	55	1000	-80	72	228.804	4	7	0
Sb	ppb	23	1000	-80	88	206.834	0	0	0
Bi	ppb	45	1000	-88	88	223.062	4	6	0

APPENDIX 3

Trace Metal Blank Concentrations (μg/g)
for the Sequential Extraction Procedure

LEAD Batch		Pore Water	AEC 1st Step	AEC 2nd Step	AEC Total	ORG 1st Step	ORG 2nd Step	ORG Total	RED 1st Step	RED 2nd Step	RED Total	Total
	1	0	N/A	3	3	N/A	0	0	N/A	BD	BD	N/A
	2	BD	BD	0	0	BD	2	2	BD	1	3	4
	3	BD	BD	BD	BD	BD	2	2	BD	1	1	3
	4	BD	1	BD	1	BD	BD	BD	BD	0	0	0
	5	BD	BD	BD	BD	BD	N/A	BD	BD	0	0	0
	6	BD	BD	0	0	BD	N/A	BD	BD	0	0	N/A
	7	BD	BD	BD	BD	2	2	4	0	1	1	6
	8	BD	1	BD	1	1	0	1	1	1	2	4
	9	0	BD	1	1	BD	0	0	4	3	6	7
	10	1	BD	BD	1	0	0	0	1	3	4	5
	11	BD	BD	BD	BD	BD	1	1	BD	5	5	6
	12	BD	BD	0	0	BD	1	1	BD	5	5	6
Avg		0			1			1			3	4
Std Dev		0			1			1			2	2

ZINC Batch		Pore Water	AEC 1st Step	AEC 2nd Step	AEC Total	ORG 1st Step	ORG 2nd Step	ORG Total	RED 1st Step	RED 2nd Step	RED Total	Total
	1	0	N/A	1	1	N/A	13	13	N/A	4	4	N/A
	2	0	0	310	310	BD	2	2	8	0	8	320
	3	BD	BD	0	0	BD	BD	Bd	BD	BD	BD	0
	4	BD	1	0	1	BD	BD	BD	0	1	1	2
	5	BD	1	0	1	0	0	1	2	1	3	5
	6	BD	1	0	1	0	N/A	0	BD	0	0	N/A
	7	BD	1	1	2	0	0	1	0	0	0	3
	8	1	1	BD	1	8	BD	8	BD	BD	BD	9
	9	BD	1	2	3	BD	1	1	1	0	1	5
	10	BD	1	3	3	BD	BD	BD	1	1	1	5
	11	BD	BD	2	2	BD	BD	BD	BD	2	2	5
	12	BD	BD	0	0	BD	0	0	BD	1	1	2
Avg		0			1.43*			3			2	3.78*
Std Dev		1			1.03*			5			2	2.32*

*Excludes Batch 2

APPENDIX 3 CONTINUED

Trace Metal Blank Concentrations (μg/g)
for the Sequential Extraction Procedure

NICKEL			AEC			ORG			RED			
Batch		Pore Water	1st Step	2nd Step	Total	1st Step	2nd Step	Total	1st Step	2nd Step	Total	Total
	1	0	N/A	1	1	N/A	1	1	N/A	BD	BD	N/A
	2	BD	BD	0	0	BD	BD	BD	BD	BD	BD	0
	3	0	1	0	1	0	0	0	0	BD	0	1
	4	0	BD	1	1	BD	0	0	BD	BD	BD	1
	5	BD	1	0	1	BD	BD	BD	0	BD	BD	1
	6	BD	1	0	1	BD	BD	BD	BD	BD	BD	1
	7	BD	0	0	1	BD	N/A	BD	BD	BD	BD	N/A
	8	BD	0	0	1	BD	0	0	BD	BD	BD	1
	9	0	0	1	1	0	BD	0	BD	BD	BD	1
	10	BD	0	0	0	0	0	0	0	0	1	1
	11	BD	BD	0	0	0	1	1	1	3	3	5
	12	BD	BD	2	2	BD	0	0	BD	0	0	2
Avg		0			1			0			0	2
Std Dev		0			0			1			1	1

CHROMIUM			AEC			ORG			RED			
Batch		Pore Water	1st Step	2nd Step	Total	1st Step	2nd Step	Total	1st Step	2nd Step	Total	Total
	1	0	N/A	0	0	N/A	24	24	N/A	1	1	N/A
	2	BD	BD	BD	BD	12	12	24	0	1	1	25
	3	BD	BD	0	0	BD	26	26	BD	3	3	29
	4	BD	BD	0	0	13	6	19	0	1	1	20
	5	0	0	0	0	12	11	12	1	1	1	25
	6	0	0	0	0	13	N/A	N/A	0	0	1	N/A
	7	BD	0	0	0	11	3	23	1	1	1	25
	8	0	0	0	1	13	26	26	0	1	1	28
	9	0	0	0	0	12	26	26	1	1	2	27
	10	BD	0	1	1	13	26	26	0	1	1	28
	11	BD	BD	1	1	BD	23	23	BD	1	1	26
	12	BD	BD	1	1	BD	23	23	BD	1	1	25
Avg		0			0			24			1	26
Std Dev		0			0			2			0	3

BD indicates concentration was below detection.
N/A (no value recorded or error)

APPENDIX 3 CONTINUED

Trace Metal Blank Concentrations (µg/g)
for the Sequential Extraction Procedure

COPPER Batch		Pore Water	AEC 1st Step	AEC 2nd Step	AEC Total	ORG 1st Step	ORG 2nd Step	ORG Total	RED 1st Step	RED 2nd Step	RED Total	Total
	1	0	N/A	BD	BD	N/A	1	1	N/A	BD	2	N/A
	2	0	BD	1	1	0	1	1	4	0	4	6
	3	BD	BD	4	4	BD	2	2	BD	5	5	10
	4	BD	BD	0	0	BD	BD	BD	2	BD	2	2
	5	BD	BD	0	0	BD	BD	BD	3	2	6	6
	6	BD	0	1	1	1	N/A	N/A	BD	BD	0	N/A
	7	BD	BD	1	1	2	2	4	0	1	1	6
	8	BD	BD	BD	BD	1	1	2	BD	0	2	4
	9	BD	1	2	3	0	2	2	0	0	1	6
	10	BD	BD	BD	BD	1	1	3	BD	2	2	5
	11	BD	BD	BD	BD	BD	3	3	BD	1	1	4
	12	BD	BD	0	0	BD	4	4	BD	2	2	6
Avg		0			1			2			2	6
Std Dev		0			1			1			2	2

BD indicates concentration was below detection.
N/A (no value recorded or error)

APPENDIX 4

Major Element Concentrations (μg/g) for the Sequential Extraction Procedure

		AEC			ORG			RED			
Magnesium	Pore	1st	2nd		1st	2nd		1st	2nd		
Batch	Water	Step	Step	Total	Step	Step	Total	Step	Step	Total	Total
1	1	N/A	33	33	N/A	12	12	N/A	9	9	N/A
2	BD	17	15	32	25	175	200	157	139	296	528
3	3	BD	29	29	BD	20	20	BD	32	32	81
4	BD	13	15	29	BD	BD	BD	2	4	6	35
5	BD	14	19	33	BD	BD	BD	2	42	44	77
6	BD	14	16	29	9	N/A	9	5	3	7	N/A
7	<1	13	14	27	6	9	14	4	1	5	46
8	BD	15	15	30	14	9	23	BD	3	3	56
9	94	15	13	28	8	10	18	6	1	7	53
10	BD	16	25	41	10	10	20	BD	10	10	71
11	N/A	BD	35	35	BD	13	13	BD	7	7	N/A
12	<1	BD	53	53	BD	15	15	BD	6	6	74
Avg	8			33			39			36	113
Std Dev	28			7			58			83	156

		AEC			ORG			RED			
Calcium	Pore	1st	2nd		1st	2nd		1st	2nd		
Batch	Water	Step	Step	Total	Step	Step	Total	Step	Step	Total	Total
1	8	N/A	236	236	N/A	107	107	N/A	13	13	356
2	BD	124	124	248	102	733	835	672	654	1326	2409
3	16	BD	247	247	BD	135	135	BD	99	99	482
4	2	105	117	222	55	24	79	91	105	195	497
5	3	111	143	254	139	97	236	89	215	303	794
6	BD	85	131	216	110	N/A	BD	108	80	188	N/A
7	2	103	118	220	101	176	277	139	88	228	725
8	3	124	107	231	129	83	212	73	113	186	628
9	434	114	131	245	100	122	222	103	35	138	605
10	2	141	202	343	158	148	306	87	214	301	950
11	N/A	BD	277	277	BD	276	276	BD	202	202	755
12	2	BD	186	186	BD	297	297	BD	265	265	747
Avg	40			244			249			287	813
Std Dev	143			39			202			337	555

BD indicates concentration was below detection.

APPENDIX 4 CONTINUED

Major Element Concentrations (μg/g) for the Sequential Extraction Procedure

		AEC			ORG			RED			
Manganese Batch	Pore Water	1st Step	2nd Step	Total	1st Step	2nd Step	Total	1st Step	2nd Step	Total	Total
1	BD	N/A	1	1	N/A	0	0	N/A	1	1	N/A
2	BD	0	0	1	0	1	1	1	1	2	3
3	<1	0	1	1	0	0	0	0	1	1	2
4	BD	0	0	1	0	0	0	0	0	1	2
5	BD	0	0	1	0	0	0	0	0	1	2
6	<1	0	0	0	0	N/A	0	0	0	1	N/A
7	BD	0	0	0	0	0	0	1	0	1	2
8	<1	0	0	1	0	0	0	0	0	1	2
9	3	0	0	1	0	0	0	0	0	1	2
10	BD	0	1	1	0	0	0	0	1	1	2
11	N/A	0	1	1	0	1	1	0	1	1	N/A
12	<1	0	1	1	0	1	1	0	1	1	3
Avg	2			1			0				2
Std Dev	1			0			0				1

		AEC			ORG			RED			
Iron Batch	Pore Water	1st Step	2nd Step	Total	1st Step	2nd Step	Total	1st Step	2nd Step	Total	Total
1	BD	N/A	BD	BD	N/A	9	9	N/A	18	18	27
2	BD	BD	BD	BD	5	13	18	10	14	24	42
3	<1	BD	BD	BD	BD	5	5	BD	14	14	19
4	BD	BD	BD	BD	5	9	14	8	5	13	28
5	<1	BD	BD	BD	15	13	28	6	5	12	40
6	<1	BD	BD	BD	14	N/A	N/A	4	4	8	N/A
7	<1	BD	BD	BD	12	14	26	5	2	7	33
8	BD	3	BD	3	9	8	18	4	4	8	28
9	22	BD	BD	BD	10	14	24	8	3	11	35
10	BD	BD	BD	BD	10	10	20	3	8	11	31
11	N/A	BD	BD	BD	BD	13	13	BD	10	10	22
12	BD	BD	69	69	BD	17	17	BD	12	12	98
Avg	2			36			18			12	38
Std Dev	8			47			7			5	22

BD indicates concentration was below detection.

APPENDIX 5

Determination Limits for the Sequential Extraction Procedure

Trace Metals (microgram/gram)

	AEC	Organic	Reducible	Total
Pb	2.40	3.90	6.80	6.90
Zn	3.10	11.90	7.00	7.00
Ni	1.20	1.50	3.00	3.90
Cu	3.90	4.10	5.30	6.40
Cr	0.80	6.70	1.40	7.90

Major Elements (microgram/gram)

	AEC	Organic	Reducible	Total
Mg	21	174	249	468
Ca	117	606	1011	1665
Mn	3	-	-	3
Fe	141	21	15	66

Determination limits are 3 times the standard deviation of the blank concentrations.

APPENDIX 6

Detection Limit Ranges for the Sequential Extraction Procedure

Trace Metals

Pb	0.4	17.1
Zn	0.3	7.4
Ni	0.2	6.7
Cu	0.3	63.0
Cr	0.1	2.8

Major Elements

Mg	2.1	120.8
Ca	2.0	70.3
Fe	26.4	291.8
Mn	0.0	1.3

APPENDIX 7

Grain-size Data for the St. Clair Delta, Lake St. Clair and the Detroit River

						Silt								Clay				
		Sand	192 to	128 to	96 to	64 to	48 to	32 to	24 to	16 to	12 to	8 to	6 to	4 to	3 to	2 to	1.5 to	
Size (% Microns)		>192	128	96	64	48	32	24	16	12	8	6	4	3	2	1.5	1	Total
Sample	Weight																	
WI-5	210.0	8.8	26.4	18.1	6.3	5.7	3.9	4.7	4.4	4.1	3.6	4.3	2.7	2.5	2.2	0.7	1.6	100.0
LS9	100.0	0.0	2.0	10.4	8.8	18.2	7.6	7.8	7.5	8.3	4.9	6.6	4.4	4.8	4.1	1.5	3.1	100.0
LS8	195.0	10.3	30.8	5.4	3.6	7.1	2.8	4.4	3.8	5.6	4.5	6.4	4.0	4.3	3.7	1.2	2.1	100.0
LS24	201.0	5.7	16.9	14.6	3.8	2.2	4.4	5.9	6.9	7.5	6.4	7.5	5.1	5.0	4.1	1.3	2.7	100.0
LS21	301.0	16.0	47.7	19.4	2.3	0.8	1.7	2.0	1.9	1.6	1.3	1.4	1.1	0.9	0.8	0.3	0.8	100.0
LS20	100.0	0.0	0.0	13.8	15.2	29.1	10.5	6.2	4.0	3.8	3.0	4.1	2.6	2.7	2.3	0.7	2.0	100.0
LS19	208.0	5.2	15.5	15.0	8.3	11.8	5.7	4.0	5.2	5.4	4.7	5.8	3.9	3.6	3.0	0.9	2.0	100.0
LS18	100.0	2.5	7.4	7.1	8.3	19.2	11.9	11.4	5.9	5.0	4.0	4.7	3.5	3.3	2.7	0.8	2.3	100.0
LS17	100.0	0.0	0.0	3.0	2.9	21.6	11.9	21.9	7.9	8.6	3.6	6.3	3.0	3.6	2.5	1.1	2.1	100.0
LS16	100.0	2.9	8.7	19.9	16.7	20.9	5.0	3.0	4.6	3.9	2.6	3.4	2.3	2.0	1.7	0.6	1.8	100.0
LS10	86.0	5.3	15.8	0.2	1.6	7.4	5.8	10.5	7.2	8.4	6.1	8.2	5.4	6.5	5.5	2.0	4.1	100.0
DT33	100.0	3.9	11.7	3.6	2.5	7.1	6.4	8.6	8.4	9.4	6.1	9.1	5.9	6.6	5.5	1.8	3.4	100.0
DT31	164.0	1.3	3.8	4.2	4.0	8.0	6.3	9.0	9.2	10.1	7.9	10.0	6.6	7.1	5.9	2.0	4.6	100.0
DT32	100.0	2.0	5.7	5.5	6.8	14.1	9.0	10.9	9.0	8.6	6.0	6.7	3.9	4.1	3.6	1.2	2.9	100.0
DT30	100.0	1.9	5.4	6.3	4.7	7.2	5.9	8.8	8.7	9.2	7.8	9.1	6.3	6.8	5.7	1.9	4.3	100.0
DT29	100.0	0.0	0.0	1.5	2.7	7.7	7.4	11.2	10.9	12.2	9.3	11.2	6.9	7.2	5.9	2.0	3.9	100.0
DT28	100.0	7.3	21.6	14.9	4.3	2.6	3.9	5.5	5.3	6.8	5.3	5.9	4.3	4.4	3.9	1.2	2.8	100.0

APPENDIX 8

SEDA and LKSD-4 Trace Metal Concentrations (µg/g)
from the SEQ Procedure

LEAD

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	52.0	45.0	45.0	143.0
	6	50.0	N/A	37.0	N/A
	6	50.0	N/A	35.0	N/A
	8	47.0	46.0	44.0	137.0
	8	48.0	47.0	41.0	136.0
	10	53.0	N/A	51.0	121.0
	11	54.0	50.0	46.0	149.0
	12	54.0	43.0	38.0	134.0
Average		**51.0**	**46.0**	**42.0**	**137.0**
Std Dev		**3.0**	**3.0**	**5.0**	**9.0**
Rel Std		**5.0**	**6.0**	**13.0**	**7.0**
LKSD	3	46.0	29.0	27.0	102.0
	3	46.0	27.0	21.0	95.0
	4	42.0	20.0	19.0	81.0
	4	38.0	30.0	23.0	91.0
	7	44.0	N/A	17.0	N/A
	8	45.0	30.0	17.0	92.0
	9	49	31	19	99
	10	49	N/A	22	N/A
	11	43	33	23	100
	12	49	32	21	101
	13	52	24	18	94
Average		**46**	**29**	**21**	**95**
Std Dev		**4**	**4**	**3**	**7**
Rel Std		**9**	**14**	**15**	**7**

APPENDIX 8 CONTINUED

SEDA and LKSD-4 Trace Metal Concentrations (µg/g)
from the SEQ Procedure

ZINC

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	103.0	168.0	177.0	448.0
	6	93.0	N/A	210.0	N/A
	6	97.0	N/A	193.0	N/A
	8	101.0	223.0	223.0	547.0
	10	94.0	N/A	N/A	N/A
	11	104.0	195.0	194.0	494.0
	12	95.0	179.0	176.0	450.0
Average		**98.0**	**191.0**	**195.0**	**485.0**
Std Dev		**5.0**	**24.0**	**18.0**	**46.0**
Rel Std		**5.0**	**13.0**	**9.0**	**10.0**
LKSD	3	54.0	25.0	90.0	169.0
	3	62.0	28.0	89.0	180.0
	4	59.0	20.0	69.0	147.0
	4	57.0	22.0	74.0	153.0
	7	59.0	N/A	60.0	N/A
	8	67.0	82.0	28.0	177.0
	9	18	73	N/A	N/A
	10	21	N/A	103	N/A
	11	64	25	90	179
	12	71	26	72	169
	13	61	91	N/A	N/A
Average		**54**	**43**	**75**	**168**
Std Dev		**18**	**29**	**22**	**13**
Rel Std		**33**	**67**	**29**	**8**

APPENDIX 8 CONTINUED

SEDA and LKSD-4 Trace Metal Concentrations (μg/g)
from the SEQ Procedure

NICKEL

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	15.0	48.0	49.0	113.0
	6	15.0	N/A	43.0	N/A
	6	15.0	N/A	41.0	N/A
	8	22.0	52.0	53.0	126.0
	10	17.0	N/A	48.0	N/A
	11	17.0	52.0	50.0	118.0
	12	15.0	48.0	48.0	111.0
Average		**16.0**	**50.0**	**47.0**	**117.0**
Std Dev		**2.0**	**20.0**	**4.0**	**7.0**
Rel Std		**15.0**	**4.0**	**9.0**	**6.0**
LKSD	3	4.0	4.0	15.0	23.0
	3	4.0	4.0	15.0	22.0
	4	4.0	2.0	16.0	22.0
	4	3.0	4.0	15.0	21.0
	7	4.0	N/A	12.0	N/A
	8	3.0	4.0	17.0	24.0
	9	4	4	12	20
	10	5	N/A	16	N/A
	11	4	3	14	20
	12	3	4	16	24
	13	5	3	N/A	N/A
Average		**4**	**4**	**15**	**22**
Std Dev		**1**	**1**	**2**	**1**
Rel Std		**18**	**24**	**11**	**7**

APPENDIX 8 CONTINUED

SEDA and LKSD-4 Trace Metal Concentrations (µg/g)
from the SEQ Procedure

CHROMIUM

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	8.0	56.0	78.0	142.0
	6	8.0	N/A	65.0	N/A
	6	8.0	N/A	63.0	N/A
	8	7.0	57.0	83.0	147.0
	10	8.0	N/A	74.0	N/A
	11	8.0	56.0	80.0	144.0
	12	8.0	51.0	73.0	132.0
Average		**8.0**	**55.0**	**74.0**	**141.0**
Std Dev		**0.3**	**3.0**	**7.0**	**6.0**
Rel Std		**4.0**	**5.0**	**10.0**	**5.0**
LKSD	3	1.0	BD	5.0	6.0
	3	1.0	BD	5.0	6.0
	4	1.0	BD	8.0	9.0
	4	1.0	BD	6.0	7.0
	7	1.0	BD	5.0	6.0
	8	1.0	BD	10.0	10.0
	9	1	BD	6	7
	10	1	BD	7	8
	11	0	BD	8	8
	12	0	BD	7	7
	13	1	BD	5	6
Average		**1**		**7**	**7**
Std Dev		**0.3**		**7**	**1**
Rel Std		**37**		**22**	**19**

APPENDIX 8 CONTINUED

SEDA and LKSD-4 Trace Metal Concentrations (μg/g)
from the SEQ Procedure

COPPER

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	26.0	52.0	50.0	128.0
	6	22.0	N/A	47.0	N/A
	6	22.0	N/A	44.0	N/A
	8	20.0	49.0	45.0	114.0
	10	18.0	N/A	59.0	N/A
	11	24.0	58.0	58.0	139.0
	12	25.0	53.0	55.0	133.0
Average		**22.0**	**53.0**	**51.0**	**129.0**
Std Dev		**3.0**	**3.0**	**6.0**	**11.0**
Rel Std		**12.0**	**6.0**	**12.0**	**8.0**
LKSD	3	BD	6.0	7.0	13.0
	3	BD	6.0	BD	6.0
	4	BD	5.0	BD	5.0
	4	BD	7.0	8.0	15.0
	8	BD	6.0	9.0	15.0
	9	BD	5.0	13	18
	10	BD	N/A	12	N/A
	11	BD	4.0	10	14
	12	BD	5.0	9	14
	13	BD	3.0	7	13
Average			**5**	**9**	**13**
Std Dev			**1**	**2**	**4**
Rel Std			**19**	**22**	**34**

APPENDIX 9

SEDA and LKSD-4 Mg, Ca, Mn, and Fe
Concentrations from the SEQ Procedure

MAGNESIUM

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	8305	16863	16866	42034
	6	9017	N/A	13438	N/A
	8	9139	N/A	13262	N/A
	8	7920	17815	17843	43578
	10	7685	N/A	17794	N/A
	11	9595	15469	15479	40542
	12	8748	15364	15370	39481
Average		**8630**	**16378**	**15722**	**41409**
Std Dev		**690**	**1177**	**1895**	**1785**
Rel Std		**8**	**7**	**12**	**4**
LKSD	3	514	23	2114	2652
	3	515	23	2068	2607
	4	518	31	2260	2809
	4	498	33	2037	2568
	7	520	17	1615	2152
	8	526	5	2891	3422
	9	569	11	1532	2112
	10	605	N/A	2190	N/A
	11	536	12	2392	2940
	12	561	25	2124	2710
	13	546	N/A	1635	N/A
Average		**537**	**20**	**2078**	**2663**
Std Dev		**31**	**9**	**390**	**396**
Rel Std		**6**	**47**	**19**	**15**

CALCIUM

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	18240	19871	19965	58077
	6	18782	N/A	17388	N/A
	6	18819	N/A	17095	N/A
	8	16978	22752	22513	62063
	10	16659	N/A	22425	N/A
	11	20362	21098	21103	62563
	12	19280	21780	21853	62913
Average		**18446**	**21330**	**20335**	**61404**
Std Dev		**1292**	**1144**	**2285**	**2245**
Rel Std		**7**	**5**	**11**	**4**

APPENDIX 9 CONTINUED

SEDA and LKSD-4 Mg, Ca, Mn, and Fe
Concentrations from the SEQ Procedure

CALCIUM

LKSD	3	6823	597	637	8056
	3	6809	561	675	8045
	4	6711	597	666	7975
	4	6526	749	603	7878
	7	6766	416	504	7686
	8	6861	579	823	8263
	9	7775	445	599	8819
	10	8011	N/A	754	N/A
	11	7177	518	687	8381
	12	7541	494	701	8736
	13	7653	365	589	8607
Average		**7150**	**532**	**658**	**8245**
Std Dev		**507**	**110**	**87**	**383**
Rel Std		**7**	**21**	**13**	**5**

MANGANESE

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	309	319	319	947
	6	295	N/A	267	N/A
	6	293	N/A	267	N/A
	8	284	352	353	989
	10	284	N/A	349	N/A
	11	333	334	334	1001
	12	334	310	310	955
Average		**305**	**329**	**314**	**973**
Std Dev		**21**	**18**	**35**	**26**
Rel Std		**7**	**6**	**11**	**3**
LKSD	3	259	27	105	391
	3	259	26	110	395
	4	250	24	115	389
	4	252	30	105	388
	7	259	23	91	374
	8	261	26	148	435
	9	303	22	90	414
	10	300	N/A	124	N/A
	11	284	28	125	437
	12	291	25	122	439
	13	298	19	96	413
Average		**274**	**25**	**112**	**408**
Std Dev		**21**	**3**	**17**	**23**
Rel Std		**8**	**13**	**15**	**6**

APPENDIX 9 CONTINUED

SEDA and LKSD-4 Mg, Ca, Mn, and Fe
Concentrations from the SEQ Procedure

IRON

Analyte	Batch	AEC Total	O Total	R Total	Total
SEDA	1	2148	27830	27821	57799
	6	1954	N/A	22303	N/A
	6	1892	N/A	22472	N/A
	8	1851	30694	30738	63283
	10	1884	N/A	29911	N/A
	11	2100	26977	26987	56064
	12	2182	24897	24900	51979
Average		**2002**	**27599**	**26447**	**57281**
Std Dev		**138**	**2403**	**3365**	**4686**
Rel Std		**7**	**9**	**13**	**8**
LKSD	3	272	3479	10654	14405
	3	282	3322	11063	14667
	4	255	3210	11469	14934
	4	231	3317	9877	13425
	7	273	2970	8744	11987
	8	257	3170	16486	19913
	9	297	2949	8602	11848
	10	304	N/A	10990	N/A
	11	241	3133	11821	15915
	12	293	3077	11863	15233
	13	232	2735	8483	11450
Average		**267**	**3136**	**10914**	**14306**
Std Dev		**26**	**216**	**2241**	**2449**
Rel Std		**10**	**7**	**21**	**17**

APPENDIX 10

Precision and Accuracy of SY-4 and LKSD-4
in the Total Fusion Determination

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
SY-4	47.55	20.01	6.04	0.52	7.74	6.07	1.69	0.29	0.11	0.31
	48.69	20.05	6.10	0.54	7.86	6.03	1.70	0.28	0.11	0.31
Average	48.12	20.03	6.07	0.53	7.80	6.05	1.70	0.29	0.11	0.31
St Dev	0.81	0.03	0.04	0.01	0.08	0.03	0.01	0.01	0.00	0.00
% RDS	1.70	0.10	0.70	2.70	1.10	0.50	0.40	2.50	0.00	0.00
Certified	49.90	20.69	6.21	0.54	8.05	7.10	1.66	0.30	0.11	0.13
% Difference	3.0	3.2	2.3	1.9	3.1	14.8	-2.1	0.7	-1.9	-136.6
LKDS-4	38.97	5.31	3.90	0.90	1.75	0.76	0.81	0.30	0.06	0.76
	40.96	5.42	4.02	0.94	1.83	0.74	0.83	0.31	0.06	0.76
	40.23	5.45	3.99	0.92	1.80	0.79	0.82	0.31	0.06	0.78
	39.92	5.22	3.92	0.90	1.76	0.75	0.83	0.30	0.06	0.83
	39.42	5.38	3.95	0.91	1.79	0.77	0.81	0.30	0.06	0.85
Average	39.90	5.36	3.96	0.91	1.79	0.76	0.82	0.30	0.06	0.80
St Dev	0.76	0.09	0.05	0.02	0.03	0.02	0.01	0.01	0.00	0.04
% RDS	1.90	1.70	1.20	1.80	1.80	2.50	1.20	1.80	0.00	5.20
Provisional	41.60	5.90	4.10	0.90	1.80	0.70	0.80	0.40	0.10	0.30
% Difference	4.1	9.2	3.5	-1.6	0.8	-8.9	-2.5	24.0	40.0	-165.3

APPENDIX 11

Raw Diffraction Data

Sample DT28		Relative Intensities					
D-Spacing	Untreated	AEC-1	AEC-2	OR-1	OR-2	R-1	R-2
18.62719		14					
15.96781			21				
14.26666				8			
14.04007					5		
13.71338		16					
12.83732			22				
12.54592		14					
10.72134		11	20				
10.28526	1						
10.17882			22				
10.05169				13			
9.99495		12			8		
9.07331		20					
7.70170			16				
7.46832		23		11			
7.32048			43				
7.19586		22	45	16			
7.08108	7				6		
6.76297		21	35				
6.37492		28	32	16			
6.19292	6						
6.17573			24				
6.12893		23					
5.96862			31				
5.71576		12					
5.50734			19				
5.35520		13					
5.26357			20				
5.05493	7		29	10			
4.63320							
4.59987	6	16	24	11			
4.52778		20	25				
4.47128		19		8			
4.45129	8				6		
4.36461			30				
4.25086			25				
4.12397	19	39	44	28	22	16	Quartz
4.04965			26				
3.99567		9	26	7	5		
3.93452			27				
3.77619			27				
3.68518	5	10					

APPENDIX 11 CONTINUED

Raw Diffraction Data

		Relative Intensities						
Sample DT28	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**	
3.56168		13	15	6		5		
3.52557	5			12	5			
3.46483						6		
3.34339	100	100	100	100	100	100		Quartz
3.24191			17					
3.19632	8				9	6		
3.13574		7		13				
3.03752	4		11					
2.99173		5	26	9				
2.80479	18	17	18	26	20			
2.77429		9	14					
2.67354		10	19	5				
2.65125			18					
2.59828	3			8				
2.562286	3	9	20		4	6		
2.544679	4							
2.477383			22					
2.460325				7				
2.453831								Calcite
2.406249		9						
2.323028			16					
2.282829	5	10		8	7	5		Quartz
2.236607			18		4			
2.194890	4							Dolomite
2.149903		9						
2.130537				8				
2.128142	5		14		6	7		
2.116256		10						
2.061584	3		14					
1.998530	3		10		4			
1.988568			14	10				
1.979935	4				4	3		
1.956113			15					
1.905768			12					
1.877629		6	12					
1.819576	9		17					
1.817879		16		16	11	8		
1.814494								
1.801096	5							
1.797781		11			5			
1.786284	3							

APPENDIX 11 CONTINUED

Raw Diffraction Data

		Relative Intensities					
Sample DT28	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**
1.701646			11				
1.672671	2			5			
1.662888	2				2		
1.657632			10				
1.605541		9					
1.585588			13				
1.553732		10					
1.541961		11	10	8	8		
1.517905		8					
1.502350	3						
1.484172		7	14				
1.473387		8					
1.451757	2	8					
1.442718		6					
1.427948					2		
1.406931		8					
1.382140	3			6			
1.374111	5	13		9	6	5	
1.349003		6					
1.333981	3	9					
1.329882	2	7					

Sample DT32		**Relative Intensities**					
D-Spacing	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**
14.742560	2						
14.382730		4	4				
14.040070				3			
10.225850			5				
10.051690	3	7		3			
9.938842							5
7.762354				4			
7.138008		4					
7.109431			16				
7.081082	4			9			3
6.107893		3					
5.905267			5				
4.995562				5			3
4.743728			5				
4.516361		4					
4.493707			10				
4.482466							5

APPENDIX 11 Continued

Raw Diffraction Data

Sample DT32

	Relative Intensities							
D-Spacing	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**	
4.258933	24	22	16	19				Quartz
4.248852							23	
4.029685	9							
3.776193	4	4	11					
3.532458		5	8					
3.525573	3							
3.343387	100	100	100	100			100	Quartz
3.196315		10		10				
3.185122							7	
3.157490	16		13					
2.986839	13	37	7					
2.887827			21	31	6		7	Dolomite
2.673541	35	3						
2.562286	3		10					
2.486672	4		7					
2.453831								Calcite
2.415609	12		7					
2.280054		6	3	7			6	Quartz
2.233950	7							
2.192338	4	5	4	6				
2.189792	7							
2.128142		5	6	5			5	
2.056684			5					
2.013265	7	5	5					
1.973819			7					
1.911053	4							
1.872182	5			9				
1.816185	3	8	12				9	
1.802759	3	5						
1.783029	12							
1.714628	11							
1.672671	7							
1.541961	3	9	8	7			6	
1.502350	10							
1.372342			6	7				
1.357532	2							
1.338112	5							

APPENDIX 11 CONTINUED

Raw Diffraction Data

Sample LS09			Relative Intensities				
D-Spacing	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**	
16.084060						3	1	
14.866540	2							
10.285260			1					
10.051690	7							
9.994945		4						
7.138008	10							
7.081082		4	4					
5.715758								
5.052070				9		3	9	
4.258933	18	25	24					Quartz
4.248852								
4.066133								
3.808097				28		13	28	
3.532458	8							
3.343387	100	100	100	100		100	100	Quartz
3.207588	17							
3.190708		14	9					
3.031462	11							
2.991730		3	4					
2.887827	24	36	27					Dolomite
2.693075				2			2	
2.453831			1					Calcite
2.428209	7							
2.282829		6	5	2				
2.125753		6	8					
1.937969				2				
1.816185	13	9	9					
1.802759		7						
1.783029			3				6	Dolomite
1.565714				5			5	
1.541961								
1.540795			5					
1.539631	8	9						
1.370579	7							

Sample LS18			Relative Intensities				
D-Spacing	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**
16.084060						4	7
14.500700	2						
14.266660				3			
14.152460		8	5				

APPENDIX 11 Continued

Raw Diffraction Data

Sample LS18		Relative Intensities					
D-Spacing	**Untreated**	**AEC-1**	**AEC-2**	**OR-1**	**OR-2**	**R-1**	**R-2**	
10.051690			10	9				
9.994945	4	25	13					
9.667545					3	2		
7.762354								
7.109430	7	22						
7.081082			15	11				
6.150112						2		
6.128929					2			
5.066401					6			
4.995562	4							
4.981634		10	9					
4.493707	4							
4.258933		22	18	19				Quartz
4.248852	20							
4.066133	9							
3.181616						8		
3.808097					29			
3.776193								
3.617275					3			
3.532458		17	13					
3.343387	100	100	100	100	100	100		Quartz
3.241908			13	3				
3.190708	12	12	12	8				
3.124979								
3.064360	16							
3.001562		9						
2.883281	34	12						Dolomite
2.453831	6	6						Calcite
2.302459								
2.280054	7	3		5				Quartz
2.233950				4				
2.125753	6							
1.992292		9	7	3				
1.979935								
1.939923								
1.817879		8	7	7				
1.816185	10							
1.802759			6					
1.562097					3	4		
1.540795	7		6					
1.371490	6							

APPENDIX 11 CONTINUED

Raw Diffraction Data

SampleWI-5			Relative Intensities					
D-Spacing	Untreated	AEC-1	AEC-2	OR-1	OR-2	R-1	R-2	
16.382240		7						
14.500700		15	2		8			
14.266660							9	
13.820570						5		
10.987580					9			
10.051690	4		17				11	
9.994959					16	10		
9.311769		12						
8.589547						8		
7.865605		10						
7.499884		15						
7.138008		10						
7.109431	7				16			
7.081082			17					
7.052960						10	19	
6.915656						5		
6.393256						6		
6.325043		8						
6.236341			18					
5.964617					12			
5.827961		11						
5.715758					12			
5.697480		13						
5.371321					11			
5.009569	2							
4.995562			11					
4.981634						11		
4.258933	20	23	28		20	23	35	Quartz
3.646482							14	
3.511887	5				8			
3.399804								
3.343870	100	100	100		100	100	100	Quartz
3.241908	7		14					
3.230385		10						
3.190708	7	12			7			
3.185122			9					

Sample WI-5			Relative Intensities					
D-Spacing	Untreated	AEC-1	AEC-2	OR-1	OR-2	R-1	R-2	
3.087911			6					
3.031462	7							
2.878751	34	9			11			
2.816841	10	39						Dolomite

APPENDIX 11 CONTINUED

Raw Diffraction Data

Sample WI-5			Relative Intensities					
D-Spacing	Untreated	AEC-1	AEC-2	OR-1	OR-2	R-1	R-2	
2.457073								Calcite
2.447372								
2.280054	6	11						Quartz
2.233950			6					
2.128142	5	10						
2.123370					8			
1.990221		8	6		8			
1.979935								
1.814494	2							
1.804425			5					
1.540795		8	6					

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